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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE EIGHTY-SECOND GENERAL MEETING of the Institution of Petroleum Technologists, to which members of the Institution of Automobile Engineers were invited, was held at the Royal Society of Arts, John Street, Adelphi, London, W.C., on Tuesday evening, January 6th, 1925, Dr. W. R. ORMANDY occupying the Chair.

The Chairman, at the opening of the meeting, said he was very pleased to say that the President of the Institution, Mr. Herbert Barringer, was rapidly recovering from his recent illness and hoped to be able to attend the next meeting.

The following paper was then read :—

The Behaviour of Lubricating Oils under Oxidising Tests.

By J. B. HOBLYN, F.I.C., A.R.C.S. (Member).

THERE is no need to emphasise the difference between the lubrication of a heavily-worked high speed internal combustion engine and machinery lubrication as accepted in the ordinary sense. In the latter type, the lubricant after use remains approximately of the same composition and is possessed of almost the same physical characteristics as when new. In short, the choice of the oil needs no consideration of constitutional changes during use. If such behaviour held in internal combustion engine lubrication, the problem would be considerably simplified, but here we have to face the fact that oils recommended by firms who have devoted a large amount of attention to the subject are still found wanting—wanting in the sense that changes occur in both the physical and chemical properties of the oil that in many cases very quickly render it so different in character from the oil originally used that these properties can in no wise be stated in terms of those possessed by the oil when new.

Some oils, of course, are better than others, and notwithstanding the belief of some people that any oil will behave quite as

satisfactorily as one more highly refined, the fact remains that any oil will not. It may do so in the case of engines that are not called upon to work at full load, but for the type of engine that goes all out, careful consideration must be given to the choice of the lubricant. It therefore seemed to the author that the suggestion made to him that a short paper be given preparatory to a joint discussion of this subject by user and supplier was sound, and he hopes that facts will come to light that will benefit both industries concerned.

Now what is the problem before us? The engineer and the car owner desire a lubricant of suitable viscosity that gives easy starting in winter, freedom from asphaltic deposits in the crankcase, a minimum of "carbon" deposit on the pistons and no oiling of the plugs. There must be no sticking of pistons and valves. The nearer the oil comes to maintaining its initial physical and chemical characteristics after use, the better it is for its purpose. Alteration in composition invariably leads to the formation of asphaltic bodies due to the action of the air and the high temperatures to which the oil is submitted, and when in this partially-decomposed condition, the viscosity in the cold state is invariably much greater than that of the oil with which we started. Observation of a large number of oils points toward the fact that those that form asphaltic bodies quickly are those possessing a low flash point, and in these cases the quick decomposition of the oil in the crankcase, producing a great amount of trouble in the starting of the engine on cold mornings, is accompanied by a partial distillation of the oil, some of the more volatile constituents being driven off and recondensing on the sparking plugs. Many, many instances could be given where this dual behaviour has quickly taken place, and it is evident in such instances that an unsuitable oil has been used. It is also evident that the initial cold test on the original oil is not of much value if that oil is going to change quickly in its constitution.

Although these alterations in properties cause troubles such as have been indicated, further trouble is caused—trouble of a far-reaching nature and rendered not the less dangerous because it is frequently overlooked. This is the loss in the efficiency of the engine due to friction, which is further due to the pudding that acts as the lubricant for a considerable time after the engine starts, particularly in wintry weather. "She pulls well after running about ten minutes" is almost a slogan. These frictional losses are now receiving something of the attention they deserve, and in these days of increasing activity in getting a high power-to-weight ratio, when designers can afford to neglect nothing, it follows that this question will be increasingly studied. These losses, although recognised, have not up to recently been considered as being

serious in magnitude, but Mr. Pomeroy in a paper before the S.A.E. last year showed that they could reach astounding figures and that they are of a far higher order than is generally supposed. (Pomeroy, *Journal S.A.E.*, Vol. 14, 1924.)

Experience shows that all oils on the market do begin at some time after use to form asphaltenes, and it appears to the author that it may be taken as axiomatic that the oil which changes most slowly is the one that deserves our most urgent consideration.

The question now arises as to how far the engineer and the car owner can be accommodated with what they want. It does not seem out of place to discuss the position as it is to-day, and to see how far the oil suppliers can give them oils approximating to their desires. In certain aspects the oil industry is very much alive, and not the least of these aspects is its ability to advertise. Thus the car owner, reading that every make of oil is the one most suitable for his own particular engine, and finding himself in a quandary, very often seeks the advice of the engineer as to what oil he should use, and the engineer has such a variety to choose from that fair advice is often very difficult. It may be said at the outset that it would be unfair to expect that the engineer is able to do prolonged engine and car tests upon the manifold varieties of oils that are on the market, for that would involve a big expenditure of time and labour; and if, on the other hand, he approaches the oil supplier, the latter in his turn has not carried out tests upon the similarly manifold varieties of engines that are on the market. This again would entail considerable time and expenditure. Thus, failing the ability of both oil supplier and automobile manufacturer to give these joint tests, resort must be made on the part of the engineer to collaboration with the supplier, and from physical and chemical tests to judge which oils he considers most suitable for his purpose and then to put them to extended trial. It is, in short, imperative for him to interpret to-day the behaviour of an oil from physical and chemical date supplied to him. Now what are these physical and chemical data required? Can we specify tests that are so sound that we can interpret the behaviour of a lubricant with that confidence that is the only justification for specification?

The importance of the necessity for such tests was emphasised in the 1920 Report of the Lubricants and Lubrication Enquiry Committee of the Department of Scientific and Industrial Research in Clause 7 of their recommendations of the main lines on which research is needed. In this clause they ask for the discovery of :—

> New methods of analysis which will enable the chemist when examining a lubricating oil in the Laboratory, besides determining its viscosity, specific gravity, flash point, etc., to determine the constituents of the oil . . . to measure its ability to reduce friction and to meet the conditions of speed.

load, temperature and atmosphere in which it is required to work. Much of this costly information can only be ascertained to-day by the costly method of trial.

Of all the tests that have been applied to oils to enable us to get some idea of what their behaviour in a high-speed engine will be, it is generally accepted that the results obtained on submitting the oils to some conditions comparable with those they meet in an internal combustion engine are the most valuable. These, indeed, do signify to what extent they will depart from their original properties, and while not disparaging other tests, the author wishes to draw your attention in particular to a study of that test believed by many to be the best one for discriminating between the types of lubricants under discussion. This is the evaporation test (many times referred to as the "heat" test), and the open flash point and sludge value are considered as parts of this test. Here the oil is heated in air, and changes in constitution occur. Dr. Ormandy (Proceedings I.A.E., Vol. 8, 1913–14), in a Paper on "Engine Lubricating Oils," expressed his opinion that when several oils are heated under similar conditions for a definite time at 400° F., "the oil that loses the least, while leaving a residue as little altered in character as possible, will give the best results." The author's opinion to-day coincides with that of Dr. Ormandy, but he would like to extend to some extent, and to consider in further detail, the examination of the residue. After all, it is the residue we have with us (sometimes, of course, accompanied by recondensed volatile matter on the plugs), and it is in the main the residue that gives us trouble. In Dr. Ormandy's paper the properties of the residue were broadly described; the residue either "runs slightly," "runs readily," or "does not run." In short, visible results were considered sufficient. It is now hoped to go further, and to consider how far further visible effects—effects of magnification—will help us in differentiating between oils, and to see how far certain simple microscopic observations upon oils when undergoing decomposition will help us in this direction. It must be said deliberately that this work, conducted in a simple primary way, has undoubtedly helped in discriminating between oils, and no cases have been found where a judgment of the probable behaviour of an oil in an engine based upon this test has gone wrong.

Let us now consider an interesting case. After investigating a large number, two straight mineral oils were found of very similar properties. These were as follow :—

	Oil 5.	Oil 6.
Viscosity at 140° F. (Redwood seconds)	188	195
Specific gravity	0·916	0·916
Open flash point	215° C.	215° C.
Setting point	0° C.	—6° C.

On heating 20 grammes of each oil in crucibles contained in a thermostatically-controlled oil bath at 250° C., the evaporation losses were as under :—

EVAPORATION CURVES OF OILS 5 AND 6.

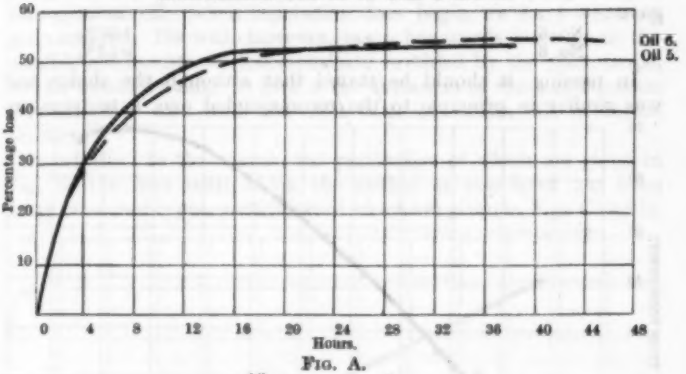


FIG. A.

Oil.	5.	6.
Viscosity	188R ..	195R
Specific gravity ..	0·916 ..	0·916
Open flash	215° C. ..	215° C.

The residue in each case after 10 hours ran very freely, and both appeared very similar to the eye. Under these circumstances, one would think that the oils would behave similarly in an engine, but on testing each in a particular car engine, after two thousand miles No. 5 had a dirty appearance in the crankcase, the contents being on the gelatinous side, the tappets were sticky, a large amount of "carbon" was on the pistons, and the dismantling of the engine revealed the fact that it was in a dirty condition. The engine was well cleaned and No. 6 oil then used. After two thousand miles the engine was comparatively clean; indeed, after allowing the fine carbonaceous dust to settle, the oil was perfectly clean, and had, singular to say, suffered no change in viscosity. There was no dilution. No. 5 was too gelatinous to allow the dust to settle. The particulars of the engine used are given on page 6.

Each oil at the start made no material difference in output at any of the stated revolutions, but unfortunately it was not possible to put the engine on the bench and obtain its output after each of these oils had been used for the mileages stated, so that evidences of frictional losses cannot be given. Sufficient evidence was forthcoming, however, to show that No. 5 decomposed in such a way as to yield very dirty oil in the crankcase, and that No. 6 remained reasonably clear. The use, then, of No. 6 would mean that less attention had to be given to the engine than with No. 5, and although unfortunately one cannot speak from fact,

it would probably render the engine freer from frictional losses, and there would be a corresponding diminution in the expenditure on petrol. The sludge value, determined by the method suggested in the recently published handbook of the Petroleum Technologists, gave :—

No. 5	1·97%
No. 6	0·53%

In passing, it should be stated that although the sludge test was similar in principle to the recommended one, a temperature

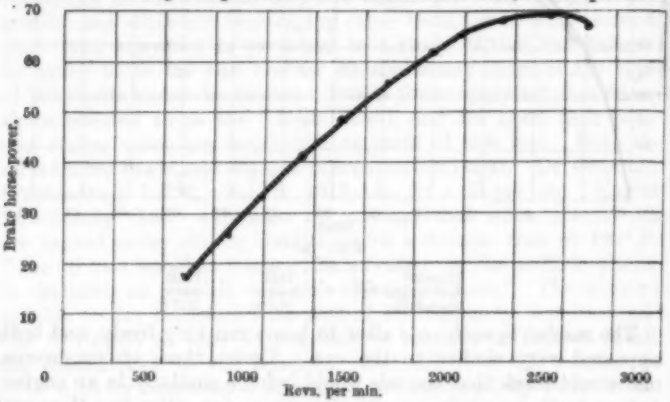


FIG. B.

23-60 H.P. 4 Cylinders, 95½ × 140 m.m. Capacity, 3·99 litres.

of 250° C. was arbitrarily fixed upon as being more drastic and more likely to find any vital differences between the oils.

Seeing that sludging gave some clue to the differences in the two oils, and seeing that sludging renders insoluble the asphaltenes produced, it was considered that it might be interesting to try to follow the decomposition of these oils microscopically. Asphaltenes are insoluble in petroleum ether. Are they also insoluble in the higher paraffinic hydrocarbons that are constituents of lubricating oils ? Are they, then, insoluble in the unchanged hydrocarbons remaining after heating ? Or, are they present in the colloidal state ? Twenty grammes of each sample were accordingly heated in crucibles and maintained at 250° C. in the oil bath, every precaution being taken to exclude dust. Small samples were then periodically withdrawn for microscopic examination. The results are shown in Plate I. Oil No. 5 began to show definite signs of decomposition in 16 hours, but Oil No. 6 was heated for 36 hours before signs of decomposition were evident. In the same Plate we see the states of decomposition when No. 5 had been heated 28 hours and No. 6 40 hours.

The author would not, under any circumstances, say definitely at the present time what these products of decomposition are. They may, in the first instance, be the separation of the asphalts, but whatever they are, until separation occurs we have physically a homogeneous oil; when separation does begin we have a heterogeneous one. He will, however, say a few words later about the possible mechanism of decomposition revealed by the microscope, but he would first like to give a few instances of the collaboration between this test and the behaviour of certain oils in actual practice.

In addition to the engine, the particulars of which are given in Fig. B, the firm with which the author is associated has been using two other types, particulars of which are given in Figs. C and D.

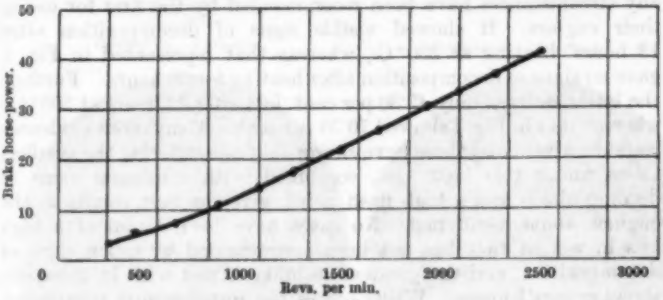


FIG. C.

14 H.P. 4 Cylinders, 75×130 m.m. Capacity 2·30 litres.

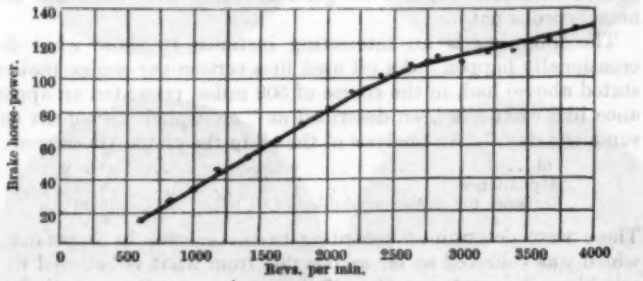


FIG. D.

30-98 H.P. 4 Cylinders, 98×140 m.m. Capacity 4·22 litres.

All three are representative of touring car engines in use all over the world to-day. They work very hard, and hence demand high qualities in lubricants. Many oil firms have recommended particular brands of oil for them, and car owners not infrequently

neglect the advice offered by the automobile manufacturer and use oils recommended by their friends. It will be interesting, therefore, to give an instance, typical of many, of oils that have been used, to show how far a reasonable theory based upon observations of the heat test would have warned owners against them. Fig. 1, in Plate II, represents the photograph of the structure at 250 magnifications of an oil recommended for two of the engines, after being heated for 30 hours at 250° C. Fig. 2 represents that of an oil heated for 25 hours at 250° C., a sample of which was sent by a car owner as a brand that had been purchased as a suitable oil but which had given him considerable trouble, particularly with "pitch" in his crankcase. The oil represented in Fig. 2 does show signs of decomposition products, and would not under any circumstances have been recommended by the firm for use in their engines. It showed visible signs of decomposition after 12 hours' heating at 250° C., whereas that represented in Fig. 1 gave no signs of decomposition after heating for 30 hours. Further, the latter suffered only 43·30 per cent. loss after 32 hours at 250° C., whereas that in Fig. 2 showed 76·70 per cent. Many more evidences could be given, and these have shown that oils suffering the smallest losses under this heat test, combined with minimum signs of decomposition and a high flash point, give the best results in the engines above-mentioned. No cases have been found of a high loss in weight that has not been accompanied by quick signs of decomposition, and the greatest stability is met with in those oils showing small losses. Where, as in the instance first mentioned, oils behave very similarly regarding loss, those showing signs of altered structure are not so good as those that maintain their homogeneous nature.

The following is an interesting instance to show what does occasionally happen. An oil used in a certain car engine (not one stated above) had, in the course of 500 miles, presented an appearance like what has been described as "an asphalt pavement on a summer's day." An analysis of the oil in the crankcase showed :—

Oil	55·26%
Asphaltenes	8·70%
Carbenes (or matter insoluble in CCl_4)	36·00%

These were determined according to the scheme in Appendix I., which was collected as far as possible from what is believed to be reliable and accepted work. If there are any points questionable, the author will be glad to have his attention drawn to them.

The word "carbenes" has been used guardedly, but whatever the name given, we have a product close upon the heels of elemental carbon.

The above analysis is mentioned as a matter of interest only. What is considered the most important fact is that a sample of

PLATE I.

Oil No. 5.

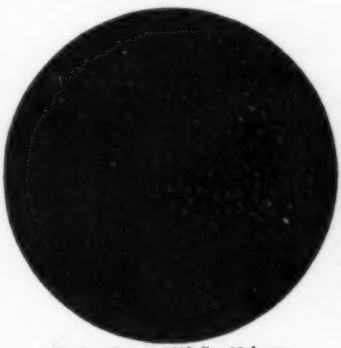
Original oil. Untreated.

Oil No. 6.

Original oil. Untreated.

After heating at 250° C. 16 hours.

After heating at 250° C. 36 hours.



After heating at 250° C. 28 hours.

After heating at 250° C. 40 hours.

250 Magnifications.

PLATE II.

FIG. 1.

FIG. 2.

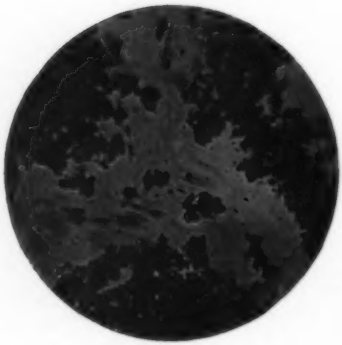


FIG. 3.

250 Magnifications.

PLATE III.

Progressive Decomposition—Oil No. 1.

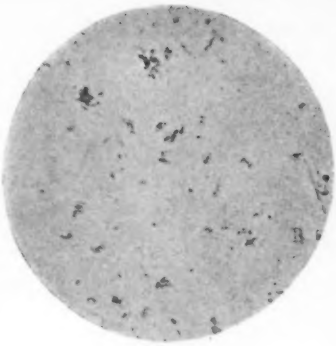


FIG. 4.
2 hours' heating.

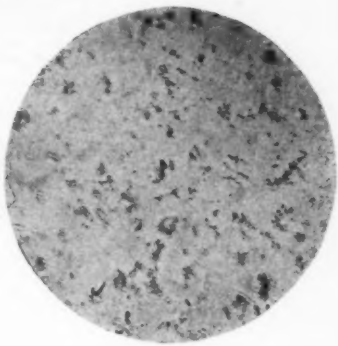


FIG. 5.
4 hours' heating.

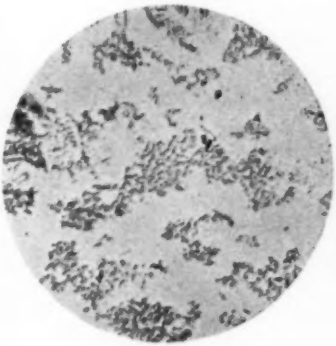


FIG. 6.
6 hours' heating.

FIG. 7.
8 hours' heating.

FIG. 8.
12 hours' heating.

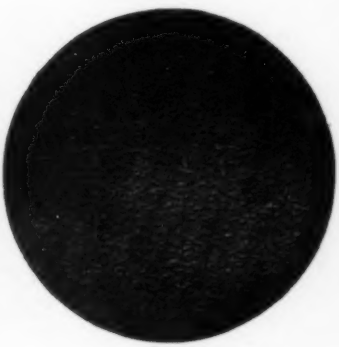


FIG. 9.
16 hours' heating.

250 Magnifications.

PLATE IV.

Progressive Decomposition—Oil No. 1 (cont.).

FIG. 10.
20 hours' heating.

FIG. 11.
24 hours' heating.

FIG. 12.
28 hours' heating.

FIG. 13.
32 hours' heating.

FIG. 14.
36 hours' heating.

FIG. 15.
40 hours' heating.

250 Magnifications.

this original oil, when submitted to the usual heat test, lost 82·90 per cent. in 32 hours, gave a sludge value of 10·96 per cent., and showed very visible signs of decomposition after 12 hours' heating. A photograph of the structure after 12 hours' heating is given in Fig. 3 of Plate II.

It will have probably been observed that the decomposition in this case seems somewhat different from that in the previous cases; and it has been stated previously that it was thought possible that the first signs of decomposition might correspond with the falling out of asphaltenes. The apparent variation in the structures, therefore, led to an endeavour as a matter of interest to follow, if possible, the changes that occur. Accordingly, a straight mineral oil that had previously shown itself to be prone to decomposition was chosen, and a series of twenty crucibles each containing 20 grammes of oil was heated at 250° C. in the oil bath. The heating was interrupted at various intervals, specimens taken and their conditions recorded after the film of oil between the cover glasses had thoroughly cooled. Before any structure was photographed, it was confirmed by five views of five different samples to make reasonably sure that decomposition was proceeding at the same rate in each crucible. After the structure had been recorded, the contents of one crucible were used for the determination of the mineral oil, soft asphalts, asphaltenes and carbenes according to the table in Appendix I. The oil chosen is referred to as No. 1, and the various structures are shown in Plates III. and IV. The following figures show the compositions of the residues at the times when heating was interrupted :—

Figure.	Time of heating.	Composition.	
4	2 hours	Soft asphalts	Nil
		Asphaltenes	0·27%
		Carbenes	Nil
5	4 hours	Soft asphalts	1·14%
		Asphaltenes	0·32%
		Carbenes	Nil
6	6 hours	Soft asphalts	2·96%
		Asphaltenes	3·65%
		Carbenes	Nil
7	8 hours	Soft asphalts	2·67%
		Asphaltenes	8·49%
		Carbenes	Nil
8	12 hours	Soft asphalts	3·10%
		Asphaltenes	14·20%
		Carbenes	Nil
9	16 hours	Soft asphalts	2·48%
		Asphaltenes	21·51%
		Carbenes	Nil
10	20 hours	Soft asphalts	2·85%
		Asphaltenes	24·36%
		Carbenes	Nil

Figure.	Time of heating.	Composition.	
11	24 hours	Soft asphalts	3·05%
		Asphaltenes	29·31%
		Carbenes	Trace
12	28 hours	Soft asphalts	2·96%
		Asphaltenes	30·10%
		Carbenes	Trace
13	32 hours	Soft asphalts	3·02%
		Asphaltenes	26·40%
		Carbenes	3·32%
14	36 hours	Soft ashpalts	3·01%
		Asphaltenes	24·82%
		Carbenes	6·12%
15	40 hours	Soft asphalts	3·28%
		Asphaltenes	23·88%
		Carbenes	7·85%

At the magnifications used (250) it was impossible to identify definitely the various constituents, but it is hoped at some future time to investigate these products in comparison with mixtures

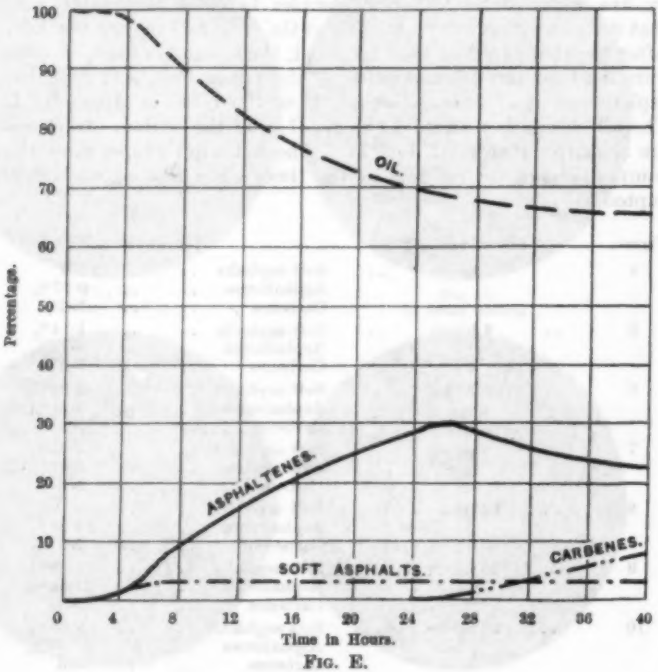


FIG. E.

of known ingredients at high magnifications, and so endeavour to elucidate the mechanism of the change. The analyses, however, showed that those asphaltenes that are soluble in carbon tetrachloride and insoluble in petroleum ether reach a maximum, and then begin to change to asphaltenes insoluble in carbontetrachloride (generally referred to as carbenes). Further progressive heating might be of some value. The curves of decomposition are represented in Fig. E.

One important fact is worthy of notice in connection with the decomposition of an oil such as that before us. We get shown clearly in the early photographs (take, for instance, Fig. 7, Plate III.) that we have at least a dual composition of the oil. We started with an oil physically homogeneous. Here it is heterogeneous. At this stage, however, its condition would still be considered good for engine lubrication, and we should not condemn it as a bad oil. Many engines, in fact, will probably be lubricated for a considerable portion of their lives by an oil represented by a similar physical condition. Hence we may not unfairly compare it with an oil homogeneous in nature; a similar oil, say, so far as initial physical properties are concerned, but one which has not yet begun to decompose—a more stable oil. Now consider these two types of oil under conditions of boundary lubrication, where we have the thinnest film possible before rupture and final seizure occur. In short, we have oils that have suffered to a greater or lesser extent by atmosphere and temperature, and we are now considering them under high speeds and heavy loads. Which film will break down first? It would seem to the author that the oil in a state of separation due to decomposition would be the one most likely, because we have gaps between them long before molecular dimensions are arrived at, but accurate experimental evidence on this point has so far been difficult to get. When seizure does occur, such a mess generally results that it is difficult to get at the real cause, but experiments are in hand to see how far the constitution of the film is responsible. It is very probable that any views that apportion the cause, or even part of the cause, to the constitution of the film of lubricant may be met with scant respect by many engineers. The automobile engineer has a "hardware" theory for seizure.

He puts it down to:—

(1) Bits of metal worn away from moving parts;

(2) Bits of metal left in the engine during assembly;

(3) Road dirt;

(4) The fact that by the failure of some mechanical device the oil does not get to its bearing.

There must, of course, be a final film in the case of (4), but this is often overlooked.

There is no need of course to contest the statement that any of the above effects would tend to cause seizure, as may also bits of carbon washed away from the piston head, but the examination of oils from certain engines in which seizure has occurred has sometimes ruled out the operation of any of the above. Over and above these causes, therefore, there seems reason to believe that failure has occurred by virtue of the fact that the lubricant has broken down, mainly on account of its heterogeneous nature. In particular, it may be mentioned that on two occasions when failure occurred in the same engine, every evidence pointed to the unsuitability of the oil. Each time the oil, when examined, was forming asphaltenes, notwithstanding the fact that each time it was comparatively new. Both the oil and the engine were reasonably clean so far as extraneous matter was concerned. It would appear that this aspect of lubrication is worthy of some attention.

It is therefore submitted that the oil that suffers the least loss, and that can be maintained a length of time at elevated temperatures without showing signs of decomposition, is the one most suitable for use in high speed engines. It best resists the joint influence of temperature and atmosphere, and it is probable that under heavy loads it maintains a film least liable to rupture. Friction losses are diminished, and the "miles per gallon" are increased.

To discuss the refining of oils is not within the province of this Paper. The engineer does not worry his head about what the oil contains, so long as it will fulfil its functions, and fulfil them well. In short, he takes the oil as the finished article, and he must judge it on its merits as such. Its constituents must therefore be selected by the oil refiner in such a way that his supplies stand up to the conditions previously adumbrated, and he must leave no stone unturned to endeavour to give the engineer those oils of great stability which the future will assuredly demand.

In conclusion, it must be said that only those types of oils sold as straight mineral oils have been considered in these notes. The castor and sperm blended oils are therefore excluded.

The author desires to tender his thanks to his Assistant, Mr. H. J. Mason, a student of this Institution, who has conducted all the experimental work referred to.

Appendix I.

The Examination of the Mineral Oil Residues.

To about 5 gr. residue add 100 c.c. petroleum spirit (B.P. 60°–80° C.), thoroughly stir, break up residue and allow to stand for 24 hours. Filter.

Soluble Portion.

1. Undecomposed oil.
2. Soft asphalts.
3. Resins and acids.

Boil off volatile spirit and dry in water oven one hour. Redissolve in 50 c.c. ether (0·72) and slowly add with continual shaking 25 c.c. alcohol (96%). Allow to stand 5 hours. Filter rapidly and wash with alcohol ether (1 : 2).

Soluble.	*Insoluble.*
Undecomposed oil. Take filtrate to dryness & weigh in tared flask.	1. Resins & acids 2. Soft asphalt. Wash well with 96% alcohol.

Soluble.	*Insoluble.*
Resins and acids. Boil off alcohol and weigh.	Soft asphalt. Extract with petroleum spirit and weigh.

Insoluble Portion.

1. Asphaltenes.
2. Carbenes.

Extract in a Soxhlet Apparatus for 3 hours with carbon tetrachlorides.

Soluble.	*Insoluble.*
Evaporate off CCl_4 and weigh until constant. *Asphaltenes.*	Dissolve in hot benzene, extract and weigh in a tared flask. *Carbenes.*

DISCUSSION.

Major A. D. Owen, in opening the discussion, said he presumed the paper was written really from the engineering point of view, although the chemical aspect had been also considered. The author had emphasised the aspect of the manufacturer, so far as blame for failures due to oil. The point of view, however, of the maintenance and operating engineer had to be borne in mind. A vehicle manufacturer might be blamed if his engine failed, and he might resent this, but the problem the vehicle user had to face was keeping his vehicle on the road every day in the week and to reduce time spent in clearing out the oil from the sump, and in repairing troubles caused by engine oil failures.

The question of lubricating oils had always been a very difficult one. An oil supplier states that his particular oil is the best, for obvious reasons; but the purchaser of the oil has no practical test whereby he can verify such statements. Hitherto we had to rely very much on the viscosity test of the oil when at normal temperatures. Some time ago he plotted curves of the viscosity

of oils at various temperatures with the object of ascertaining whether there was really anything of use in this test of viscosity, and found that at the working temperature of an I.C. engine cylinder the viscosities of the various oils are all much about the same whatever the viscosity at normal temperatures might have been. Therefore the viscosity test was of very little value.

A good many failures of engine big-end bearings occur. Some of these are obviously due to mechanical defects, but many failures are directly or indirectly connected with the oil. But the question of whether a thick oil is necessary is apropos. Some little while ago he received the results of a test of an engine oil that had run a thousand miles in a lorry engine, and was astonished at the amount of residue that was contained in that oil. The oil was put in a centrifuging machine, and the residues, whatever they were, asphaltenes or carbenes, were separated out. From less than two gallons of oil, after a thousand miles run, there were several cubic inches of solid matter. The question arises whether, if decomposition of the oil occurs, it is possible to separate out the oil which has been affected from the oil which has not been affected, and if after it had been centrifuged the apparently good residue would retain all the characteristics of the original oil. It is said that it is the same, but he had not yet received the chemical tests of the oil so that he was unable to state whether such is the case or not. It was unquestionably a fact, however, that quite a lot of solid matter was taken out from the oil. He would be much interested if the author could state whether the foregoing is borne out by his experience. If so, there appears a great deal to be said for centrifuging oil, as then engine pumps could be cleaned out far more frequently than they are at present without loss of expensive oil. That brings up another point. The custom at present is, after running a vehicle for so many miles, to add fresh oil, and continuing to do so (say) daily. As a result a vehicle does not use oil anything approaching the original, but a lot of contaminated oil together with a little of the original quality. Engines run perfectly well, and this being so the question arises whether a good oil is necessary or not as the bulk of the running is done with what is presumably an inferior mixture of oil. Some months ago he examined an engine that had very large oil passages in the crank pins. It was found that, except for a small passage, the oil ways of the crank pins were filled up with carbon which must have come from the oil and have been centrifuged by the rotation of the crankshaft.

He was afraid that very few of these remarks deal with the chemical side of the question, but they do show the need of a ready test that can be applied by a user, preferably by mechanical means, whereby he can judge one oil from the other; also whether used

oil could be again used or should be rejected. Such a test would, further, tend to reduce the appalling number of oils now on the market, many of which must be very similar.

Mr. S. E. Bowrey said that the impression prevailed that the most important quality to be sought in engine oil was that which would give maximum horse-power, and too often this quality was judged by the results of a comparatively brief test. However desirable it might be to ensure the greatest possible power output, those who had studied motor lubrication would realise that the chemical stability of the oil was a consideration of at least equal importance and one which, because it could not be readily assessed by the consumer, was often neglected.

He felt that the photographic method of recording the results of the oxidation test would prove useful where microphotography formed part of the regular routine, but that the determination of the amount of deposit insoluble in petroleum ether would prove to be a more generally useful method. He wished to ask the author what steps were necessary to avoid misconception arising merely from change in colour or from variations in the photographic process. For instance, one would expect an oil of red colour to appear darker in the photograph than a yellow oil, and although one might endeavour to disregard density and consider only the number of solid particles visible, it was conceivable that a deeply printed photograph would give an impression of greater deterioration.

Experience of a great variety of motor oils of the type commonly used for touring and commercial purposes went to show that when viscosities were equal there was but little difference in power output so long as the oil remained in new condition, but it was most important to select an oil of the right viscosity. The thickening of oil referred to by the author was not only due to deterioration, whether by oxidation or other cause; it was in many cases due to the presence of amorphous wax or vaseline and the fact needed emphasising that remarkable results could be achieved by carefully refining out this impurity. For instance, it was possible to produce, at reasonable prices, oils of fairly heavy body (equal to that of castor oil when compared with it at steam heat) which were twice as fluid as castor oil at 40° F. and which would withstand temperatures well below freezing point without solidifying.

Aside from this question of viscosity, stability tests should be the principal criterion of motor oil, and it was his experience that there were two independent factors to be investigated. First, there was the liability to deteriorate by oxidation which the author had dealt with in his paper and which could be tested either by the method described, by a form of the Michie sludge test, by the

Waters' test of the Bureau of Mines or by other methods. In the second place there was the liability to be decomposed by heat alone which could be tested by heating the oil beyond its distilling point in a neutral atmosphere and weighing the coke residue. This test, generally described as the Coke Test, gave an indication of the extent to which oil intensely heated on top of the pistons and the cylinder head would give rise to carbon deposit, and it was a noteworthy fact that certain oils which behaved well under the oxidation test were liable to form heavy coke residues at higher temperatures. The following figures would illustrate this point :—

Oil.	Approximate Redwood Viscosity at 140° F. Secs.	Coke test. (Percentage of coke residue.)	Oxidation test. (Percentage of sludge deposit.)
1	150	0·28	0·15
2	155	0·49	0·15
3	150	0·30	0·29
4	218	0·68	0·14
5	200	0·42	0·23
6	250	1·02	0·19
7	183	0·90	0·13
8	75	0·21	0·61
9	318	0·73	0·11

He maintained, therefore, that due regard should be paid to the Coke Test as well as to the oxidation test. It might be laid down as a rough generalisation that the non-oxidising quality of an oil depended mainly upon the class of crude from which it was obtained, whilst its behaviour under the Coke Test depended mainly upon the way in which it was refined.

In the past there might have been a tendency to stop the refining of oils short of the ideal point so that by leaving behind a trace of asphaltic matter the troublesome waxes might be held in solution, but to-day, with improved methods of wax extraction, this was no longer necessary and there was an increasing demand for oil carefully freed from both impurities.

Mr. E. R. Redgrove said that the paper constituted a decided step forward in the science of lubrication. The author stated in the first paragraph that "the choice of the oil needs no consideration of constitutional changes during use." With that statement he was afraid he could not agree, and he knew that others who had seen the mess that could result from using an unsuitable lubricant on, for instance, high speed ring-oiled bearings were of the same opinion. Every lubrication question needed the most careful consideration, because the amount of power which was annually lost through avoidable friction must reach an appalling total. It might be said of the tests which the author had applied to lubricating oils that they were very severe; the conditions of the tests were of a more severe nature than would ever be en-

countered in an internal combustion engine, excepting when the oil got on the piston head. But the fact that in the tests the author had been able to differentiate between oils and find out the good ones, and that in actual practice the results obtained were in agreement with the results of the laboratory tests, was to his mind a sufficient justification for the severity of the tests. Any test which would go further than the usual physical readings in proving the worth of the lubricant must receive consideration. He would have much liked to see the result of tests of more oils than were mentioned in the paper ; and on manipulative questions there were one or two points to which he would like to refer. For instance, what was the size of the crucibles used in the heating tests, or what was the surface area of the oil exposed. In Fig. E he presumed the curve marked " oil " was based upon the rate of formation of soft asphalts, asphaltenes and carbenes. He thought it would have been instructive if, on that same figure, the evaporation curve of the oil had been included. The author had stated that he used a controlled oil bath, and that the crucibles were suspended on a copper gauze grid. He would very much like to know how creeping was prevented. Personally he had found that the use of a double crucible did a lot to overcome the difficulty. Important as the paper was—and, no doubt, it would have far-reaching effects, because car manufacturers would soon be alive to the fact that the lubricant which they recommended must be of the highest quality procurable if the best was to be obtained from their products—he could not help feeling that, so far, only half the story had been told. The paper told the members how to differentiate only between pure mineral lubricating oils, how to gauge the lasting properties of pure mineral oils, in which must also be included the lubricating properties of mineral oils after they had been in use for some considerable time, but left untouched that large class which contained fatty oils or fatty acids. The germ theory of Southcombe and Wells was now fairly well established in so far as ordinary lubrication was concerned, but it was found to be very seriously wanting when the point of breakdown was near. Then only a considerable percentage of suitable fatty oil could stave off disaster. The reason of this was a subject which had always interested him, and at the present time he was conducting an investigation on the question which might, or might not, throw some light upon the subject. As there were many users of lubricating oils present he would like to ask them to be a little kind to the lubricating oil experts. He asked them, when a failure occurred, not to say immediately, as they always did at present : " It is the oil." A perfectly good clean sound oil might be sent out, but if it was stored in a careless way, so that grit and dirt found entrance, trouble would most likely follow.

He asked oil users not to believe that because an oil looked thick that it must be good; more often it was not so.

Mr. E. A. Evans said that the author had expressed the opinion, and he quoted Dr. Ormandy as also being of the same opinion, that the evaporation loss was of importance in judging lubricating oil. Personally, he was not going to say that was or was not the case, but he would say that it needed a vast amount of qualification. If the author and the Chairman still maintained their opinion he would be curious to know how the evaporation loss of, say, a mixture of black cylinder oil and paraffin would behave because it had been suggested at that meeting that it would make an admirable lubricant for internal-combustion engines. It was interesting to hear that there was a difference between one oil and another such as were used for automobile engines. He said that with a considerable amount of feeling because it had been suggested in the course of the discussion that in the past a great many people had been judging oil upon the ordinary physical data, such as gravity and viscosity. For a long time past a number of the members had been stating perfectly openly that that was quite a wrong thing to do. Those tests were very useful but they were not all in all. The opinion had been expressed at meetings of the Institution on several occasions that an oxidising test of some sort was not only desirable but absolutely imperative. The question now arose what test was going to be adopted. Frankly, he was not sure whether the test the author had put forward was going to help. It would be extraordinarily useful, if one could test an oil by heating it in a crucible and then examine it under a microscope, but those who had very much to do with the oxidation of oil in laboratories realised that the test was beset with great difficulties. The question was raised at the Institution a few years ago, and the speaker, amongst others, then stated that the oxidation test would vary with the temperature, *i.e.*, if the amount of sludge formed were plotted against temperature different curves would be obtained for different oils. It therefore seemed impossible at the present moment to say whether a sludge test should be done at one temperature or another, but it would be very laborious to make the test at a number of temperatures. At any rate he could assure the members of the Institution of Automobile Engineers that serious work was being done in connection with the oxidation test. One of the speakers had asked whether an oil lost its value when in the engine, and whether a cleaned oil was as good as new oil. The doctrine had been preached in the past that oil suffered from paresis and should be thrown away, but that, with centrifuging, an oil could be made to last a longer time. He desired to utter a warning, however, that when an oil was used in a car it would develop acid which no centrifuging

would remove. A certain amount of washing was useful in removing it, but the distinctly serious problem had to be faced of the pitting of ball races if the oil were used for too long.

Mr. G. W. Halse said the opinion seemed to be generally prevalent that carbon deposit in an engine was simply due to the oil, but he would like to ask how far that was correct. What became of the dirt and dust that were sucked into the carburetter? It went in, but did it go out again? It would be very interesting if the author could state if he had analysed the carbon deposit in engines run over average roads, and to what extent it contained identifiable road matter. Moreover, of the retained dust, that portion which did not remain in the carbon deposit adhered to the lubricating oil on the cylinder walls and, consisting of finely divided silica and other particles, acted as an abrasive. This abrasive mixed with the lubricating oil and circulated through the bearings again and again, caused additional wear; therefore any development which tended to keep the oil clean and free from foreign particles would certainly prolong the life of engine bearings and would tend to reduce the cases of blame being laid on the lubricating oil for failures which were not primarily due to the oil itself.

Dr. F. B. Thole said that while the paper was of high importance it gave the impression of being only the first introductory chapter to a study of most extensive scope. A most interesting table in the paper set out the analytical history of a sample of oil during a period of 40 hours under oxidising conditions at a high temperature. At the end of this period the oil was no doubt black in colour, but was it actually any the worse for this; in other words, has the change which has occurred in the oil reduced its friction reducing qualities? If the oil were particularly susceptible to undesirable decomposition, quite possibly it would be a worse lubricant, but if it were an oil of average good quality it was quite within the bounds of probability that it would perform its proper functions in an engine as well as the new oil. The speaker suggested that it would be most valuable to study the effect of this heat treatment under actual engine conditions; *i.e.*, to charge an engine with the oil and run it, coupled with a dynamometer, under uniform conditions for 40 hours, or preferably much longer, and compare the changes in the oil with those of the dynamometer reading at regular intervals.

A similar series of experiments had been recently carried out in America with a Buick car, and the results showed a definite improvement in the lubricating oil with use over quite a long period; only towards the end of a long trial did the power output of the engine begin to fall off. Further, if during the main period of the run, when the power output was increasing with the age of the oil, the

oil was partly replaced by fresh oil, an immediate fall in power was apparent. The slippage of gas past the piston rings also steadily fell as the oil became older.

The author had raised an important point in stating that a highly refined oil was superior to one less highly refined. While it is probably true in many cases that a light refining treatment is necessary to remove certain traces of reactive and undesirable components, after this is done, further refining, though it gives a paler and more attractive looking oil, steadily diminishes the lubricating qualities of the oil. The ultimate product of intensive refining of lubricating oil is medicinal paraffin which is a very poor lubricant indeed.

The view taken by Dunstan and Thole in a paper read before the Institution in 1918, and amply confirmed during recent years, was that the essentially valuable friction-reducing components of a lubricating oil are the unsaturated compounds, and as these are progressively removed by all ordinary refining processes the degree of refining should be cut down to the very minimum necessary.

In demanding an oil of light colour and pleasing to the eye, the user frequently gets a product of actual inferiority, just as by demanding an oil of unnecessarily high viscosity (and it is surprising how many users think high viscosity synonymous with high lubricating quality) he is actually wasting his engine power.

Mr. H. D. Nickinson said he was one of those who believed, with certain reservations, that any oil would do, and he based his belief on practical experience, and the fact that obviously all the oil producers are not selling the same oil under different names and prices.

Coming to the points raised by the author, there does not seem to be anything new in this method except the microscopical examination, and for commercial laboratories the test would take too long to perform. This question of evaporation losses has received a good deal of attention in the past, the speaker had used Archbutt's method for some time. The temperature advocated by the author seems much too high and it is doubtful if much of the lubricant reaches this zone, since if there are evaporation losses, as shown by the author, of 50 per cent., vehicles would not be able to do 1,000 miles to a gallon of oil, and 500 miles to a gallon of oil is common in many large fleets; the speaker would suggest 180° C. as a more suitable temperature. There is no doubt that engine design has a very great bearing on the behaviour of lubricants in internal-combustion engines, especially whether cast-iron or aluminium pistons are used, the system of lubrication is important, and designers would be wise to make their engines so that they can be lubricated with the cheapest oils. In particular, the system of full force feed on many engines is faulty, and the splash trough is no doubt a better

system. The speaker gave instances of an oil being satisfactory when used with splash trough feed and failing when used in a full force feed system.

Regarding an engine working hard, the speaker always understood that the average touring car was very much over-engined, and does not work nearly as hard as a 'bus engine doing 1000 miles per week, and up to 25,000 miles in six months.

Referring to the oil mentioned as having an appearance like "an asphalt pavement, etc.," the speaker would suggest that water had come in contact with this oil, as little as one per cent. would have this effect.

The speaker put before the meeting the results of some tests carried out at the N.P.L. on the Lanchester Worm Gear with three samples of oil :—

1. New oil as used on 'bus engines.
2. Dirty oil from a 'bus engine after six months' run.
3. Same oil as (2), filtered through double Whatman papers and fuel removed.

The oil (3) was badly oxidised, as the fuel was removed by heating to 160° C. and blowing with air for 1 hour.

These tests consisted in measuring the efficiency of the worm gear at various temperatures of the lubricant, from 25° to 85° C., at a speed of 1100 r.p.m. of the worm and transmitting 34 h.p. The load chosen represents a nominal mean distributed pressure on the worm wheel teeth of 1·5 tons per sq. in., calculated on the assumption that the load is taken on the whole area of the face of the tooth at once. The actual area of contact is much smaller and the intensity of the pressure correspondingly greater than these nominal values :—

	Efficiency, per cent.		
Temp. ° C.	Oil 1.	Oil 2.	Oil 3.
25 ..	94·2 ..	93·3 ..	93·6
30 ..	94·2 ..	93·3 ..	93·6
35 ..	94·2 ..	93·3 ..	93·6
40 ..	94·2 ..	93·3 ..	93·6
45 ..	94·2 ..	93·3 ..	93·6
50 ..	94·2 ..	93·3 ..	93·6
55 ..	94·2 ..	93·3 ..	93·6
60 ..	94·0 ..	93·3 ..	93·6
65 ..	93·5 ..	93·2 ..	93·4
70 ..	93·4 ..	93·2 ..	93·3
75 ..	93·2 ..	93·0 ..	93·2
80 ..	93·0 ..	92·9 ..	93·0
85 ..	92·9 ..	92·8 ..	92·9
Average efficiency % over range 25-85° C.	93·8 ..	93·3 ..	93·4

From the above figures it will be seen there is little difference in the lubricating value of the new and dirty oil.

The speaker understands that precautions were taken to prevent dirt, etc. entering the crucibles by covering them with brass gauze

covered with cotton wool; this would surely prevent the free access of air to the heated oil, and would vitiate the test as an oxidising test; also he asked whether any precautions were taken to prevent the acid fumes, from the heated samples, attacking the brass gauze and dropping back, condensed as liquid, into the heated samples.

Mr. H. Kerr Thomas said that, in connection with the remarks of the last speaker, he recently had occasion to observe the efficiency test of a worm-gear running with standard worm-gear oil, of which he had used many hundreds of gallons. It was expected that the axle would be efficient, but although it was very accurately tested it was found to have the very low efficiency of 87 per cent. Another oil was substituted, and the same axle, running under the same conditions, gave an efficiency of 96 per cent.

Mr. D. Finlayson thought the paper was of great value, as it gave definite information on a subject of which little was really known. The author appeared to make out a very good case for the advantages of co-operative research, and, as he put it, the motor engineer could not know every oil, and the oil supplier could not know every engine. The answer to the question, "What is a good oil?" ought to be welcomed both by the Institution of Petroleum Technologists and the Institution of Automobile Engineers, but an answer could only be expected by the co-operation of both groups of interests. He was glad to note the author laid such great stress on the evaporation test combined with the sludge test, and that he realised its incompleteness by modifying it somewhat. That fact had been recognised by the Research Association of British Motor Manufacturers, with which he had the honour of being associated. They had endeavoured to secure an evaporation test which would be very much closer akin to the conditions of practice. The disadvantage of the ordinary evaporation test was that it was undoubtedly very far from the conditions of practice. It was rather premature at the present moment to say very much about the results, but, as with the author's tests, there was undoubtedly an enormous difference between different brands of oil which were reputed to be suitable for the same purpose. Rather to his surprise he noted that the author still expressed his viscosity results in Redwood seconds. He would have expected the author to be one of the first to have impressed upon the automobile and the oil industries the desirability of abandoning the habit of expressing viscosities in Redwood seconds, and adopting instead the rational c.g.s. unit—the poise. Several instruments were available at the present time which gave viscosities directly in c.g.s. units. The British Engineering Standards Association had issued particulars of the standard method for determining viscosities in absolute units, and absolute units were now being freely adopted by the lubricating oil specialists in America.

He did not think there was any excuse for this country to delay the introduction of such a reform or for it to lag behind the United States. Reference was made to the increase of viscosity in lubricating oils after heating, which coincided with the formation of asphaltic bodies, and there was no doubt, he thought, that this occurred. He thought it should be remembered that some oils showed a marked decrease of viscosity on heating, and it was quite likely that the two processes might be carried on simultaneously. He desired to take advantage of the present opportunity to call attention to a misapprehension which might arise from the remarks of the first speaker in the discussion, Major Owen, who mentioned that by extrapolating some of the temperature-viscosity curves he came to the conclusion that the viscosities of all lubricating oils were exactly the same at a sufficiently high temperature. The Research Association had investigated the viscosity of lubricating oils at temperatures up to 250° C. and without exception it had been found that if oil A was more viscous than oil B at a temperature of 25° C. it was also more viscous at 250° C. Advertisements were to be seen in which two viscosity curves crossed over each other. All his experience was exactly opposite. If one oil was more viscous than another it maintained its viscosity, provided that before the measurement was started the oil was subjected to prolonged heat treatment to render it stable. Some oils lost half their viscosity on heating; others gained.

Mr. H. Moore said he regretted the author had not set out in his paper the analyses of the oils tested. In putting forward the results and stating the objectionable features of certain oils it would have been much better if the analyses had also been given so that some idea might have been formed of their respective relationships. He hoped the author would state in his reply the exact type of oil under test, because the object of the paper was to avoid the recurrence of such troubles in future, and if the information were given it would be to some extent a guide. The instability to which reference had been made must, he felt, be connected to a large extent with the wax content of the oils, because in the first place wax was the most unstable component in mineral oil. It was certainly the one that underwent cracking at the lowest temperature and it had the lowest ignition temperature. It decomposed at a lower temperature than all other petroleum products, and apart from the asphalts and asphaltenes present in the original oil, assuming it had undergone refining treatment at the beginning, he thought it was the most unstable product. The colour also would have given some idea of the method of refining and the amount of asphaltic bodies which might be expected to be present in the oils. He had made a large number of analyses of oil samples before and after centrifugal

treatment. As a general rule centrifugal treatment extracted all the matter which was out of solution and left in anything which was in solution. Asphalts, which were in solution, remained in; any inorganic material and precipitated asphalts would be thrown out. The great difficulty in employing centrifugal treatment for oil had nothing to do with arrangements connected with the centrifuge but with the collection of the oil. Small quantities of oil were available all over the country, but it was found that to collect the oil, centrifuge it, and transport it in barrels would cost probably more than the oil was worth afterwards. Except in special cases in which large quantities were available at a particular spot the use of centrifuges was limited by that fact. It was quite a mistake to say, as the last speaker had done, that viscosity-temperature curves did not cross over. He could bring forward oils which showed that, whatever preliminary treatment was given to them, the viscosity-temperature curves would cross over to the extent that one oil at 70° F. would be three times as viscous as another, and would be considerably lower in viscosity at 200° F. There was a tendency for the viscosity curves always to point towards a certain direction as the viscosity became lower. That led one to think it was the same point, but it was simply an error of the instrument and was not the true reading of the viscosity of the oil. A substance absolutely devoid of viscosity would give a reading of about 17 seconds in a Redwood viscometer. this period being in no way connected with the viscosity, but being the time required for the substance to fall through the viscometer according to the law of falling bodies. Thus, at elevated temperatures, as the viscosity of oils becomes lower, they begin to approach this figure, and though the actual viscosities may be widely different, they appear to be approaching one constant quantity. One or two points that had been brought forward rather indicated that there was a lot of use in the old-fashioned test that the lubricating trade used. The usual test was gravity, viscosity and flash-point. The flash-point was very closely related with the evaporation except in special mixtures. One was practically a function of the other. The gravity was an indication of the base and the viscosity gave the quality and the type of oil for different lubricating purposes.

The following communication received from **Dr. V. Henny** was then read:—

Regarding the comparative tests, I should like to know whether the engine was cleaned before testing oil No. 5, as this cleaning is specially mentioned before testing oil No. 6?

Further, whether it was ascertained that the gasoline used during the road tests was absolutely the same for each test? Dilution of crank-case oil is a factor not to be overlooked.

Regarding road tests, I should like to point out that dust plays a very important *rôle* in deterioration of lubricating oil in the motor-car, dust which is soaked in with the air. I have seen excellent lubricating oil made at the Shell Co. of California become very dirty and gelatinous after driving only 200 miles on dusty mountain roads in California.

In view of this, I am rather sceptical about the value of comparative tests on lubricating oils obtained from tests on the road.

Dr. W. R. Ormandy said that, using adequate quantities and renewing the oils at sufficient frequent intervals, any oil could be made to do, but the question of the ultimate viscosity within the ranges generally employed was not a matter of great importance because all the engine oil got fairly hot and ultimately fairly thin. The tests described by the author interested him very much because they related in a sense to a continuation of work which he (the Chairman) started a long time ago. He thought it would be interesting to find out whether a sample of what would be classed by the author as a bad oil would, if placed in an atmosphere of oxygen, absorb the oxygen more rapidly than a sample of what would be classed by the author as a good oil. For that purpose Mr. Craven designed a little instrument consisting of a small glass flask with a tube through it containing some bad and some good oil, and oxygen was blown through. The flask was then sealed and kept for a period of 60 days and the absorption of oxygen calculated in cubic centimetres. It was an extraordinary thing that, under those conditions, the bad oil was steadily absorbing less oxygen than the good oil. It was of course quite impossible to draw a conclusion from a single test, but the ratio of absorption remained reasonably steady. The experiments were done at ordinary laboratory temperature. It was then thought it would be very interesting if the experiment were carried out at a higher temperature, and they therefore tried heating the oil in a flask and bubbling air through it, putting a reflux condenser on the top, thinking that they might weigh the amount of gain due to the absorption of oxygen. Unfortunately, however, the reflux condenser did not condense adequately. But the experiment did show that instead of having to wait for 40 hours for the bad oil to show really serious deterioration, it was possible by bubbling air through a sample, heated only to 200° C. for 10 hours, to get one oil which was very considerably acted upon and one which was comparatively little acted upon.

It was sufficient to say that there was a very considerable difference in the two oils after heating ten hours at 200° C. The point that struck him as being of the greatest interest in the paper was that, whether the members agreed or not that oil which had suffered

such a change was very much worse in regard to its utilisation as a lubricant, what it was desired to know was whether the property of forming such insoluble bodies was characteristic of types of base oils. Would what was known as an asphaltic oil when heated under those conditions, even after complete refining, tend, under oxidising conditions, to continue to form asphaltic bodies? Would an Appalacian oil, a real straight Pennsylvanian oil, tend less to form those bodies? That type of investigation must be carried out in its relationship to base oils. It was necessary to find out first of all whether a given base oil could or could not be made to stand that test. If it was afterwards found that the test was really applicable in regard to the durability of oils in a crankcase, the user of oils at least knew which base oils to use where they were called upon to perform very heavy service. The mean pressures were exceedingly high in the engines which had been used, and the engines ran very hot. The problem in regard to lubrication was undoubtedly vastly more severe in the case of one of the engines referred to than it would be in a motor 'bus engine, in which the mean pressure on the piston was probably not much more than half the mean pressure which obtained in the particular cases referred to in the paper.

Before calling upon the author to reply very briefly to the discussion, which he would have an opportunity of replying to at length in writing, he desired to assure him that the members of the Institution were very much indebted to him for having placed before them a study on a subject from the point of view of a man who was not biased, but who was anxious to find out a means of testing an oil rapidly in the laboratory so that it might be known how it would behave under very difficult conditions in the engine.

Mr. J. B. Hoblyn, after thanking the Chairman for his remarks and the members for the manner in which the paper had been received, said he would reply in writing to most of the points raised during the discussion. So far as the question of viscosity was concerned, he was not going to be drawn into any argument. The fact that two able experimenters had differed very considerably in the views they had expressed regarding viscosity at high temperatures led him to think that he had adopted the right line. He would like to say, however, that the viscosity of the oil at high temperatures was in many cases absolutely beside the point. What we had to compare was the viscosity of the oil at high temperatures with the viscosity of pitch at the same temperature. It was foolish to infer that because an oil had a particular value at 200° C., in a decomposed condition the viscosity of the mess produced would be exactly the same. Users should be warned against employing oils that are too thin in pumps with leaky pistons and in engines with too great clearances. Reference had already been made to the

remark imputed to the Chairman that "any oil will do." He wrote the paper at the suggestion of Dr. Ormandy with the intention of pointing broadly to the troubles met with by the engineer and car owner and of submitting some simple test for the discrimination of oils for internal-combustion engine practice. He had been taken to task for not using absolute units for viscosities; but he might, perhaps, be permitted to state that it was his original intention to do so, but he was dissuaded on the plea that statutory units in this country were Redwood seconds, and that these were generally used. Mr. Bowrey had drawn attention to the discrepancy existing between the evaporation losses and the coke test in many oils. This was most interesting, coming from one who had had so great an experience. In the oils that had been tested by himself, both by the coke test and by the evaporation test, he did not think any big divergence had been noticed.

Dr. Thole's remarks were exceedingly interesting, and would be dealt with in greater detail later.

The following contributions to the Discussion were subsequently received:—

From **Mr. E. H. Cunningham-Craig**:

In Mr. Hoblyn's interesting and important paper the point that appeals most forcibly to geologists is the microscopic study of oil-films and the effects of high temperatures upon them. It is evident that there is much to be learnt by microscopic examination that might be overlooked if only chemical methods are employed.

The results of heating, as shown in Mr. Hoblyn's figures, exhibit a very marked resemblance to the phenomena of the deterioration of the globules in a torbanite. First of all there is a darkening of the material, and this is followed by the gradual breaking up of homogeneity, till finally the compounds of greater molecular weight are distinctly separated out from the body of the material. In fact, there is a more or less complete resolution of the colloid.

In a torbanite globule there is, of course, a percentage of inorganic matter which in the latter stage of deterioration becomes apparent, but the oil content of a torbanite globule has very much the ultimate chemical composition of a lubricating oil, and therefore the effects of long continued heating might be expected to be somewhat similar to those figured in the paper. These effects are no doubt to some extent due to the loss of lighter fractions, and in the case of torbanites this has been proved by many retorting tests of seams in which the globules show under the microscope distinct deterioration: the further this process has gone, the heavier the resultant crude oil.

Seven years ago the writer made a series of experiments upon microscopic slides of fresh torbanite by subjecting them to temperatures ranging from 250° C. to 350° C. for several hours. Rapid distillation of oil at the higher temperatures masked the final effects and made it very difficult to ascertain exactly what had happened, but the earlier effects were very clear—first a darkening of the gels, then a gradual loss of homogeneity, a separation into darker and lighter portions, and finally some traces of the inorganic contents could be detected in spite of the slides being flooded with distilled oil.

The evidence so beautifully figured by Mr. Hoblyn adds another confirmation of the view that the globules in torbanitic seams are gels of petroleum and inorganic matter.

From **Mr. B. D. Martin:**

During the discussion a speaker, in pointing out that the paper deals only with "straight" Mineral Oils, referred to "the so-called 'Germ' Process of Wells and Southcombe." After stating that the Wells and Southcombe theory was "fairly well established," this speaker suggested that it might be "found wanting when the breakdown point is reached." No evidence was given to justify this suggestion, which in point of fact is not correct.

An independent authority, DR. T. E. STANTON, reporting practical work done at the National Physical Laboratory, writes * :—

> The effect of adding 1 per cent. fatty acid to the Bayonne is to produce a marked improvement in the efficiency and to *raise* the critical point from 47° C. to 57° C.

It was interesting to be reminded by MR. HOBLYN that in the running of an automobile engine "boundary lubrication" operates.

MR. HOBLYN, in a written reply to the discussion, stated that Major Owen's experiences were extremely interesting, and indicated that unsuitable lubricants had been used. The moral was pointed that had wise discrimination been shown the nature of the trouble indicated would have been considerably minimised. He was glad to note that Major Owen laid emphasis upon the time spent in clearing unsuitable oil from the sumps and the considerable expense that naturally followed when unsuitable "pitch"-forming oils were used. Respecting the remarks of Major Owen upon viscosity, the point might be impressed that the tests on viscosities of lubricating oils at high temperatures lost a considerable amount of their value if the data obtained were indiscriminately applied to the behaviour of the oils in internal-combustion engines. The fact remained that many of these oils in hot engines did become so hot that, under the conditions of atmosphere and temperature, they

* "Friction" (Longmans), by T. E. Stanton, C.B.E., D.Sc., F.R.S., M.Inst.C.E., M.I.Mech.E., p. 134.

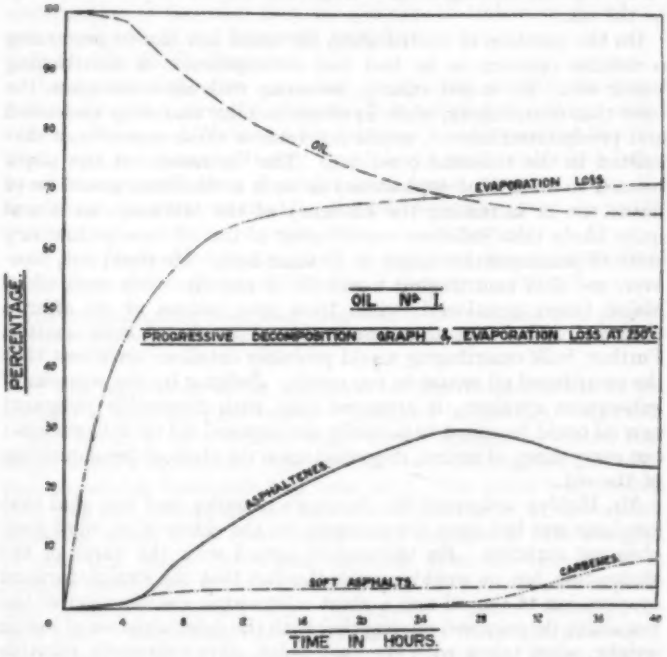
changed so much in their composition that the viscosity of the original oil was no measure whatever of the viscosity of the semi-decomposed product. He had seen oils in such a state of decomposition when taken from sumps that at 150° C. they still remained in a semi-solid condition. This might point to gross carelessness on the part of the car owner, and meant considerable abuse of the engine parts, but there could be no doubt that had oils prone to less decomposition been used such phenomena would never have been manifested. The viscosity, indeed, as Major Owen remarked, was in such cases of very little value. He was interested to note that many big end bearing failures had been due directly or indirectly to the oil.

On the question of centrifuging, he would not like to pronounce a definite opinion, as he had had no experience of centrifuging motor oils. He would submit, however, with all reservation, the view that centrifuging, while in all probability removing suspended and precipitated matter, would not remove those asphaltenes that existed in the colloidal condition. The discussion on the paper seemed to show that asphaltenes in such a condition would be of direct use in increasing the efficiency of the lubricant, so it was quite likely that judicious centrifuging of the oil in a preliminary state of decomposition might be of some help. He could not, however, see that centrifuging would be of any use with such oil as Major Owen mentioned, when from two gallons of oil after a thousand miles' run there were several inches of solid matter. Further, bulk centrifuging would probably entail so much cost that the centrifuged oil would be too costly. Judging by the remarks of subsequent speakers, it appeared that with reasonable judgment new oil could be added to partially decomposed old oil with success ; but everything, of course, depended upon the state of decomposition of the old.

Mr. Hoblyn welcomed Mr. Bowrey's remarks, and was glad that emphasis was laid upon the necessity for the choice of an oil of good chemical stability. He thoroughly agreed with the value of the sludge test, but he would impress the fact that the straightforward evaporation of the oil and a short microscopic examination of the remaining decomposed oil, together with the determination of loss in weight, when taken with the flash point, gave extremely valuable information. With some oils as little as six hours' heating at 250° C. yielded a considerable loss in weight, and the residue showed signs of decomposition to an extent that would condemn the oil at once for use in the engines for the lubrication of which he was responsible. This would involve only four weighings, simple preparation of a specimen for microscopic view, and during the rest of the time the experiment was taking care of itself. In point of total time taken, he very much questioned whether the evaporation test as given in

the paper took up as much time as the performance of a "sludge value." Mr. Bowrey's remarks respecting the photographic method of recording the results were perfectly correct, but it might be as well to state that photographic results were very rarely taken, but had had to be done in the present instance to give members a general idea. In ordinary practice a view of the sample under investigation was quite sufficient, and in such cases the darkening of the oil rarely interfered in the visual examination. It would be as well to

PROGRESSIVE DECOMPOSITION GRAPH AND EVAPORATION LOSS AT 250° C., OIL No. 1.



record that the darkening of the oil was, of course, distinct from decomposition in the sense that decomposition produced suspended asphaltenes. Naturally Mr. Bowrey had far more experience in the examination of lubricating oils by ordinary laboratory methods than had he (Mr. Hoblyn), but it might be said that all the oils mentioned in the paper were subjected to the Conradson Coke Test, and in every case this test confirmed the evaporation and decomposition findings. There could, of course, be no doubt whatever as

to the value of the Coke Test, and the last thing desired was that any inference should be drawn that would suggest it was in any way minimised.

Mr. Hoblyn appreciated Mr. Redgrove's remarks, and was sorry that his lack of knowledge on the lubrication of high-speed ring-oiled bearings caused him to omit this and kindred considerations. The crucibles used in the heat tests had a capacity of 60 c.c., and the surface areas of the oils exposed were approximately 17 sq. cm. The oils compared in the paper varied remarkably little in specific gravities, so that, as the same weight was taken in each case, the areas were approximately the same. In Fig. E the curve marked "Oil" represented the amount of unchanged oil present. The amounts represented on the curves of the various components in the partially decomposed oil at any time should be approximately 100, the departure from this figure being, of course, an analytical error. At Mr. Redgrove's suggestion, the evaporation loss was here incorporated.

He felt there could be no doubt that in future commonsense would teach motorists to buy much thinner oils, but the engineers who recommend these oils must take care that they are not prone to quick decomposition.

Mr. Evans seemed to be in a peculiarly non-committal vein, and although he (Mr. Hoblyn) had not performed any experiments whatever upon a mixture of black cylinder oil and paraffin, he would submit the opinion that the evaporation loss, the flash point, the nature of the residue and the sludge value would condemn it as a lubricant for the engines he mentioned, and he submitted, further, that the use of such a mixture in such an engine would be followed by disastrous consequences. It was obvious that the failures of cars could frequently be put down to the car-builder. What was to be impressed was the fact that it was often the case that, due to the injudicious use of oil which quickly decomposed, the owner of a car, dissatisfied with its behaviour, began to interfere with the engine, as amateurs were prone to do, and by so doing put it hopelessly out of tune. He then blamed not the oil, the prime cause of trouble, but the car manufacturer. Whether the test advocated was going to help or not, would, of course, have to be left to the verdict of extended trial; but it had helped him, and helped him well—in fact, helped him more than any other test—in the discrimination between lubricating oils; and the better behaviour of the oils in engines so far as gross inconvenience to owners had been concerned had justified it.

Mr. Halse's observations referred in the main to the road dirt that was sucked in with the incoming air and to the disadvantages attendant on the same. Many "carbon" deposits upon piston tops had been examined, and the minimum mineral matter found

had been 1·66 per cent. and the maximum 3·12 per cent. Such an amount would certainly have a deleterious effect upon bearings, etc., and it was also submitted by some investigators that it had an accelerating effect upon the decomposition of the oil, taking up the *rôle* of a catalyst.

Dr. Thole drew attention to the fact that after forty hours' heating under oxidising conditions at a high temperature one of the samples of oil was black in colour, and he asked if it actually were any the worse for this. It was not only black in colour, it contained precipitated asphaltenes; and although it might be conceded that sound experimental evidence was still lacking, he (Mr. Hoblyn) believed it *would* be worse from a friction reducing standpoint. At, say, a quarter-way point, it might be none the worse, but in such a condition as had been shown its consistency, even at elevated temperatures, was very thick. Such oils as this produced excessive trouble, and the hope was expressed in the paper that subsequently some experimental evidence—evidence on the lines suggested by Dr. Thole—might throw light upon the extent of the friction losses when quickly decomposable oils were used. It did appear from the general statements that had been made, and particularly in view of the evidence given by Dr. Thole respecting the experiments recently conducted on a Buick car, that we might get a certain amount of asphaltenes produced, that these asphaltenes might still remain as colloids, and that up to a certain point they did keep down friction as well as, or perhaps even better than, the new oil itself; but no evidence was given by Dr. Thole respecting the condition of the oil when it began to increase in its lubricating value. It looked as though the oil were an exceedingly good one, and not the type that was so often used by motor-car owners.

It was refreshing to note that Mr. Nickinson now "believed with reservations" that any oil would do, so one might look forward to the day when he would be convinced that any oil would not do. It might be well to remind Mr. Nickinson that nothing new was claimed for the test, and his attention might further be drawn to the reply to Mr. Bowrey respecting the time taken in its performance. It would have been interesting to have had more details from Mr. Nickinson as to why oils that were satisfactory when used with a splash trough feed failed when used in a full force feed system. It looked as though the quality of the oil might have been of vital significance. The cases of excessive decomposition that had been mentioned in the paper had not been due to the influence of water, and no case was known in connection with the engines referred to where 1 per cent. of water had produced pitch to the extent that had been met with. In fact, oils had been examined which, due to engine defects, had contained up to 15 per cent. of water, possessing no gelatinous nature whatever. The tests men-

tioned by Mr. Nickinson conducted at the N.P.L. on the Lanchester Worm Gear were interesting, and he (Mr. Hoblyn) could also provide oils that would behave very similarly. He could also produce oils that would not. He was appalled to think what the efficiency would have been if the particular worm gear had to plough its way, even at 85° C., through some of the material he had seen. The experiment would have been far more interesting had Mr. Nickinson given the compositions of the new oil, the dirty oil and the filtered oil. It seemed obvious on the face of it that an excellent oil had been used.

When it was stated during the meeting that pains were taken to exclude dust by covering the copper container with gauze over which was placed cotton wool, it was not meant to lead anyone to infer that the crucibles had a piece of brass gauze put right on the top of them, and the manner in which so many oil investigators at the present time spoke about " acid fumes from oil " was noted with alarm. Perhaps Mr. Nickinson at some future date would state the nature of these acid fumes and give one an idea to what extent they are produced. It seemed a pity that the word " acid " was being as indiscriminately used by them as it was by the man in the street.

It was to be regretted that Mr. Kerr Thomas had not at his disposal particulars of the two oils which gave such a remarkable difference in the efficiency of the same axle. The figures he quoted were figures of fact, and the inference to be drawn was that any oil would not do for the purpose he had in view.

Mr. Finlayson's experience with various oils evidently confirmed his (Mr. Hoblyn's), and he was exceedingly glad to hear that the Research Association of British Motor and Allied Manufacturers were endeavouring to secure an evaporation test which would be akin to the conditions of practice. He had read with interest the Paper on Viscosities of Lubricating Oils, of which Mr. Finlayson was joint author, and desired to state how much he appreciated the quality of the experimental work that had been conducted. As, however, this work was unfortunately of a confidential nature, further discussion must be left for the moment in abeyance.

It was not considered desirable to give information in the direction that Mr. Moore required, but he (Mr. Hoblyn) had at his disposal much information respecting the analyses of the oils tested, which were, of course, at the disposal of Mr. Moore if he required them. He could not quite agree with Mr. Moore in his deductions that the instability of oils was in the main due to the wax content. His experience had always shown that oils reasonably rich in wax had a relatively high setting point, and in his experience of lubricating oils during the past few years no oil had been used that had had setting point higher than -2° C. Further, the flash-points had

always been over 400° F.—generally of the order of 420 to 450° F. It must be remembered that the oils discussed in the paper were oils that were sold as high grade lubricating oils, and, of course, were bought as such and examined with a view to finding whether they were suitable or not for automobile engine lubrication, the suitability being determined by particular laboratory tests. The origin, the refinement, etc., as was definitely stated in the paper, were considered outside its scope.

The views expressed by Mr. Moore regarding viscosity were extremely interesting, particularly in view of those that had previously been expressed by Mr. Finlayson. A joint discussion on the subject, opened by one of these gentlemen and followed by the other, would be of great interest. It did seem a pity that the straightforward, if somewhat difficult, methods of accurately determining viscosities yielded in the hands of different investigators different results.

For Dr. Henny's information it might be said that the engine was cleaned before No. 5 oil was used, and it was regretted that this statement was omitted from the text. To say that the gasoline used in each road test was absolutely the same would, of course, be going too far. It was, however, derived from the same reputable source in each case, and was taken from bulk deliveries. Samples of these bulk deliveries had given remarkably close resemblances in their distilling ranges, and the aromatic contents had varied between 19 and 22 per cent. It would, therefore, be reasonable to say that the same type of fuel was used in each test. Dr. Henny rightly pointed out the influence of road dirt, but this point had already been dealt with. The whole point he (Mr. Hoblyn) wanted to make was that two particular oils, used as an average motorist used them, differed considerably in the amount of trouble given in regard to "pitchy" deposits, and he submitted a simple way of discriminating between such oils. In no sense was the road test a quantitative comparison, but it *was* comparative in the sense that judgment was made of oils by the method of trial and observation adopted by motorists to-day, and it was sufficient to state that the judgment upon the oils in the running test confirmed the deduction drawn from laboratory experiment and observation.

Dr. Ormandy's experiments were most interesting, and it was a pity that the oxygen absorption test at the higher temperature broke down. Any attempt to shorten a test was to be commended. It must be stated, however, that forty hours were not necessary in which to form an opinion as to the relative merits of lubricating oils, for many began to show evident signs of decomposition after six hours' heating at 250° C., but on the other hand some would go thirty hours or so and show no signs of change except darkening. The point raised by Dr. Ormandy as to the behaviour of different

base oils was an important one, and it might be said that so far as investigations had gone, it appeared that the paraffin base oils were more stable so far as precipitation of asphaltenes was concerned; that asphaltic base oils quickly began to decompose and to precipitate asphaltenes; but that the asphalt base oils that had been refined, although yielding oils that were dark in colour, did not yield precipitated asphaltenes anything like so easily, although analyses of the darkened products showed that asphaltenes were undoubtedly present. It would appear, therefore, that the question to be asked was: Did the partial refining of oils rid them of any matters (resinous, etc.) that had the effect of throwing the asphaltenes out of solution? It might be that when the asphaltenes were produced from the refined oils and remained in the colloidal state, the lubrication value of the oil was somewhat improved. This was suggested, and only suggested. The real fact could only be settled by a direct appeal to experiment.

Mr. Cunningham-Craig's comments were most interesting and were very much appreciated.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE EIGHTY-THIRD GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, on Tuesday, February 3rd, 1925. In the absence of the President the chair was taken by Dr. A. E. Dunstan, F.I.C., F.C.S.

The Secretary read the list of newly-elected members as follows :—

Members.—Albert Dudley Brokaw, Josef Theodore Erb, Aubrey Hamilton Garner, H. Harper McKee, Robert Ralston Rakestraw.

Transference to Member.—Andrew Pollock Faickney, Frederic Horace Garner.

Associate Members.—Robert Leonard Green, Robert Harcus, Walter Gilbert Langford, Arthur Douglas Lumb, John William McLeod, Ian Strachan Rutherford, James Govan Smillie, Reginald Bradbury Southall, Albert George Archibald Sutton.

Transference to Associate Member.—Herbert George Austin, Ernest Leon Bass, Frank Edward James Foxall-Smedley, William Ernest Read Westmoreland.

Students.—August Frederik Hendrik Blaauw, Ronald Broadhurst, Guy Tunstall Notley, Douglas Jonathan Pull.

Associates.—Austin David Jones, Clarence Castle Smith.

THE CHAIRMAN said it was a great privilege to him that evening to welcome Prof. Waterman and his assistant, Mr. Perquin, to the Institution. It had been his good fortune on more than one occasion to have been present at Prof. Waterman's laboratories in Delft and to have seen in progress his remarkable researches on the fundamental processes of the Bergius method of hydrogenation.

He need not mention to his chemical confrères that the Delft University Laboratory was one of European renown and that the School of Petroleum Technology there had achieved international reputation.

It was a great honour to the Institution to have so distinguished a foreign member to address it that night. Prof. Waterman had been a contributor to the proceedings of the Institution and was a very active recruiting agent for the Institution in Holland.

Hydrogenation in the Petroleum Industry.

By H. I. WATERMAN, Ph.D. (Member), and J. N. J. PERQUIN (of the Technical University of Delft, Holland).

I.—INTRODUCTION.

Hydrogenation in the industry of vegetable and animal oils and fats has already been studied during a great number of years. We have to deal with a process that in the *presence of nickel-catalyst already at low temperatures proceeds with high velocity.*

Cotton-seed oil, without any catalyst, in an autoclave with hydrogen[1] at 132KG/CM² at 180° C., and shaken during three hours was not hydrogenated. This was proved by the *refraction remaining unaltered*, and by the fact that the hydrogen pressure in the autoclave did not diminish[2]. The addition of the ordinary quantity of nickel catalyst on a support of kieselguhr already at 60° C., after two hours under similar conditions (compressed with hydrogen to 124 KG/CM²) gave a substantial hydrogenation, and a hydrogenated fat of a melting-point of 57–58° C. was obtained, and the agreement in the decrease of refraction and iodine value was important.[3]

Still at 30° C., under analogous circumstances (compressed with hydrogen to 118 KG/CM²) the velocity of hydrogenation was rather high, although naturally not so fast as at 60° C.

The possibility of hydrogenating at such low temperatures apparently proves that the hydrogenation of fatty oils is a very simple process.

It has been proved that hydrogenation of fatty oils under normal circumstances may be more complicated. Not only does hydrogenation take place, but we have also to reckon with a loss of hydrogen by the nascent stearic acid during hydrogenation.[4] This is connected with the formation of isomeric oleic acids.[5] These facts may explain the different percentages of iso-oleic acid in the products of hydrogenation obtained at different methods, as being applied in a research of E. J. Lush[6] ("drip" and "overflow" method).

The study of processes occurring during hydrogenation of oils is in close connection with development of analytical methods for the investigation of the reaction products, and the possibility of transformations during analysis seem not to be excluded. So, for example, K. A. Williams and E. R. Bolton[7] describe an instance of increasing the percentage of "iso-oleic acid" by prolonged contact between the lead salts and gasoline.

Notwithstanding these complications, which are the cause of the occurring reactions at definite temperatures not yet being completely investigated, our present knowledge of the hydrogenation of fatty oils is rather extensive. This subject becomes much more

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[1] O_2-content: $\pm$ 2 per cent.

[2] It was observed that the iodine value had been lowered with some units. The oil had obtained a very disagreeable smell and taste.

[3] The O_2-content of the gases had been lowered to 0·5 per cent.

[4] Compare Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320T.

[5] Compare, too, H. I. Waterman, "The Hydrogenation of Oils, Gorinchem," 1921, and therein mentioned literature.

[6] E. J. Lush, *J. Soc. Chem. Ind.*, 1923, **42**, 219T; 1924, **43**, 53T.

[7] K. A. Williams and E. R. Bolton, "The recognition of hydrogenated oils," *The Analyst*, 1924, **49**, 460. In this paper different methods of separation of liquid and solid fatty acids are reviewed. For separation of saturated and unsaturated acids compare, too, A. Grün, *Z. f. angew. Chemie*, 1924, **37**, 939.

difficult when temperature is very high, *i.e.*, exceeding 400° C. and still higher. Then the *oil itself* undergoes very important *transformations* and even hydrocarbons are formed.

It is known that Engler, in the distillation of fish oil at 300°–400° C., under a pressure of 4–10 atmospheres, obtained about 75 per cent. of a liquid mixture of hydrocarbons[8]. Not only liquid, but gaseous hydrocarbons, and in the first place CH_4, were formed, and also CO, CO_2 and water.

In our experiments[9], carried out at 450° C., in an autoclave which was shaken continuously, pressure was much higher than in the experiments of Engler. In addition, two series of experiments (Tables A and B) were carried out. (*a*) The fatty oil (cotton-seed oil) was heated in a closed vessel. The pressure (in experiment IX more than 170 KG/CM²) was practically exclusively the result of the evolution of the gases formed at decomposition, namely CO_2, heavy hydrocarbons, CO, H_2 and methane-hydrocarbons. (*b*) Before beginning the experiment hydrogen was introduced to a very high pressure, over 100 KG/CM². The high pressure observed during the heating of the cotton-seed oil, and the final pressure after complete cooling, are caused both by the gases formed at decomposition and by the added hydrogen in so far as this is not consumed. Much hydrogen is used directly or indirectly for the formation of water.

From these experiments can be concluded that the oxygen of the cotton-seed oil is expelled almost completely after a short time (1 to 2 hours). This is illustrated by the oxygen-balances of Numbers VII and IX and of XXII and XXV.

OXYGEN BALANCE.

Experiment No. VII.

Before the experiment.	Gr.	After the experiment.	Gr.
In cottonseed oil	32·4	In gases * CO_2, CO, O_2 ..	20·5
In hydrogen (O_2 content: 2·0%) ..	2·2	In water (10 gr.)	8·9
	34·6	Total ..	29·4

Experiment No. IX.

Before the experiment.	Gr.	After the experiment.	Gr.
In cottonseed oil	32·4	In gases * CO_2, CO, O_2 ..	22·0
		In water (2 gr.)	1·8
		Total	23·8

* Leaving water vapour out of consideration.

[8] C. Engler–H. Höfer, *Das Erdöl*, 1909, **2**, 110.

[9] H. I. Waterman and J. N. J. Perquin, *Proceedings Koninklijke Akademie v. Wetenschappen*, Amsterdam, 1923-1924, **27**, 83.

No. of the experiment.	Time of heating to the required temperature (in minutes).	Duration of the experiment proper (in minutes)
VII.	40	120
IX.	35	120
XII.[1])	36	60
XIII.	35	60
XIV.[2])	35	60
XV.	33	60
XVI.	40	60
XVII.	36	5

CRACKING AND BERGINISATION OF COTTON-SEED OIL AT 450° C.

TABLE A.

Time of heating to the required temperature (in minutes).	Duration of the experiment proper (in minutes).	Initial pressure in atmospheres.	Maximum pressure in atmospheres.	Final pressure in atmospheres.	Yield from 298 gr. of cotton-seed oil used in gr. and percentage of weight.					Oil obtained.						Bromine value (addition) of the		Acid value of the		Gases obtained :												Number of litres of supplied hydrogen.	Number of litres of hydrogen still present.	Number of litres of hydrogen consumed.	Absorbed hydrogen in grammes.	Percentages of weight of hydrogen absorbed.
					Oil.	Water.	Gas.	Coke.	Loss.	Sp. gr. at ± 15°.	Acid value.	Distill according to Engler (yield in percentages of weight).[3] Gasoline to 230°.	Kerosene 230—300°.	Residue > 300°.	Loss	Gasoline.	Kerosene.	Gasoline.	Kerosene.	Quantity in litres.	Density compared with air.	Analysis[5] CO_2.	Heavy hydrocarbons.	O_2.	CO	H_2.	Other hydrocarbons.	(rest) Nitrogen.								
40	120	101	272	47·7	203 (66·0%)	10 (3·3)	68 (22·3)	5·5 (1·8)	20·3 (6·6)	0·793	5·1	60·6 (44·2)[4]	17·7 (11·7)	15·5 (10·5)	6·2	14·5	6·5	3·2	0·9	63	0·877	18·8 (24·4)	1·1 (1·4)	0·4 (0·5)	7·3 (9·5)	23·0	44·2	5·2	75 L. (8·8 gr.)	14·5	60·5	5·4	1·8
35	120	0 atmospheric pressure	171	32·0	169 (56·7%)	2 (0·7)	64 (21·5)	15 (5·0)	48 (16·1)	0·818	1·0	57·1 (35·2)[4]	17·1 (9·7)	20·8 (11·8)	5·0	16·8	8·5	0·3	1·8	51	1·022	23·8 (25·9)	2·8 (3·0)	0·9 (1·0)	10·9 (11·8)	8·0	49·9	3·7					

TABLE B.

					Used ± 200 gr. cotton-seed oil (XXII. : 200 gr., XXIII. : 204 gr., XXIV. : 200 gr., XXV. : 198 gr., XXVI. : 202 gr., XXVII. : 201 gr.); yield in gr. and percentage of weight.																													
					Oil.	Water.	Gas.	Coke.	Loss.																										
36	60	110	270	79	126 (59·3%)	8·5 (3·9)	69 (32·4)	1 (0·5)	8·9 (3·9)	0·774	0·3	67·1 (43·7)[4]	14·9 (8·8)	11·6 (6·9)	6·4	17·2	5·2	0·3	0·1	95	0·582	8·5 (18·4)	0·4 (0·9)	0·4 (0·9)	6·2 (13·4)	53·9	27·1	3·5	108 L.[6] (13·4 gr.)	51·2	56·8	5·1	2·5
35	60	110	251	85	146 (67·2%)	8·5 (3·9)	58 (26·7)	0·6 (0·3)	4·3 (1·9)	0·790	7·6	59·3 (43·4)[4]	20·8 (14·0)	15·1 (10·2)	4·8	17·0	5·0	6·3	1·2	92	0·512	9·3 (24·3)	1·0 (2·6)	0·5 (1·3)	3·7 (9·7)	61·8	20·0	3·7	108 L.[6] (13·4 gr.)	57·0	51	4·6	2·3
35	60	0	79·5	22	124 (62%)	1 (0·5)	42 (21)	14 (7)	19 (9·5)	0·817	1·3	52·9 (35·0)[4]	22·3 (13·8)	21·2 (13·1)	3·6	24·3	7·9	1·0	0·2	31	1·094	27·9 (31·2)	4·8 (5·4)	0·9 (1·0)	10·0 (11·1)	10·5	45·8						
33	60	0	81·5	21·6	132 (66·6%)	3·5 (1·7)	44 (22·2)	14 (7·1)	4·5 (2·3)	0·812	1·9	55·5 (38·5)[4]	21·0 (14·0)	21·2 (14·2)	2·3	24·0	7·9	1·9	0·3	32·5	1·077	26·4 (29·4)	4·6 (5·1)	1·1 (1·2)	12·8 (14·2)	10·3	38·2	6·6					
40	60	0	81·5	21·5	127 (63%)	3·5 (1·7)	46 (22·8)	14·5 (7·2)	11 (5·5)	0·816	2·3	55·3 (37·4)[4]	20·7 (13·0)	20·0 (12·6)	4·0	24·0	7·6	2·4	0·4	33·5	1·093	25·4 (28·2)	4·2 (4·7)	0·8 (0·9)	13·4 (14·9)	10·0	40·8	5·4					
36	5	110	222	96·5	172 (81·4%)	9·5 (4·5)	30·8 (14·6)	0·6 (0·3)	— —	0·847	36·4	19·3 (17·1)[4]	22·4 (18·2)	56·6 (46·1)	1·7	42·0	15·6	22·7	7·6	103	0·239	5·0 (33·3)	0·4 (2·7)	0·3 (2·0)	2·9 (19·3)	85·0	6·4		111·4 L.[6] (10·0 gr.)	87·5	23·9	2·1	1·0

[1]) The thermo-couple having been slid from the tube, the temperature rose in this experiment during the last 10 minutes to ± 500°.
[2]) Just before the termination of this experiment there arose a small leakage, which could soon be repaired by screwing on the reflux cooler.
[3]) The figures placed between brackets indicate the yield in percentages of weight of the initial product.
[4]) Gasoline inclusive the loss in the distillation by Engler's method.
[5]) The percentages placed between brackets have been calculated on gas free from hydrogen.
[6]) Determined experimentally.

No.	Time to reach reaction temp. (min.).
99	25
106	29
107	26
103	23
108	30
104	30
109	25
102	26
111	39
74	28
76	36
89	28
80	30
78	32
92	25
87[1]	25+27
94[1]	23+25
72	20
68	27

[1] In the
260 and 90 kg
[2] Appro
[3] CO_2 a

Readings during the Experiment.							Ingoing Material.			Product (per cent. on wax charged).				Analysis of the Liquid Product.													
															Engler Distillation.									Bromine value (addition).			
															Per cent. by weight on liquid product.					Per cent. by weight on wax charged.							
o.	Time to reach reaction temp. (min.).	Time at reaction temp. (min.).	Initial pressure (kg. per sq. cm.).	Maximum pressure (kg. per sq. cm.).	Pressure cold (kg. per sq. cm.).	Temperature during reaction (° C.).	Wax (g.).	Gas (g.).	Gas (per cent. on wax).	Oil.	Gas.	"Carbon."	Loss (calculated).	Specific gravity.	Gasoline to 220° C.	Kerosene 220°–300° C.	Residue above 300° C.	Loss.	Gasoline + loss.	Gasoline + loss.	Kerosene.	Residue.	Liquid product.	Gasoline.	Kerosene.	H
9	25	1	110	210·5	105	450°	200	11·4	5·7	99·7	6·1			—	—	—	—	—	—	—	—	—	—	—	—	—	—
3	29	1	110	218		450°	200	12·7	6·3	99·7	6·6			—	2·3	2·4	94·8	0·5	2·8	2·8	2·4	94·5	4·8	35·1	26·6	I
7	26	1	0	6·2	0·6	450°	200	0	0	99·3	0·7			0·884	2·5	2·9	94·2	0·4	2·9	2·9	2·9	93·6	7·5	59·2	41·0	
3	23	15	110	220	106·5	450°	200	12·4	6·2	98·5	7·7			—	9·3	8·4	81·7	0·6	9·9	9·7	8·3	80·5	8·2	30·0	16·9	I
8	30	15	0	14·3	2·7	450°	200	0	0	96·8	2·2	0	1·0	0·831	15·1	12·2	71·4	1·3	16·4	15·9	11·8	69·1	19·6	57·4	26·0	
4	30	30	110	223	104	450°	200	12·7	6·3	94·5	9·2		2·6	0·819	20·3	14·3	64·2	1·2	21·5	20·3	13·5	60·7	12·8	25·0	13·1	I
9	25	30	0	28·4	4·8	450°	200	0	0	92·5	4·3		3·2	0·781	28·2	16·3	52·8	2·7	30·9	28·6	15·1	48·8	25·1	47·6	20·8	
2	26	45	110	219	100	450°	200	12·7	5·3	94·3	9·2		2·8	0·755	30·6	18·0	48·8	2·6	33·2	31·3	17·0	46·0	10·5	23·5	12·3	I
1	39	45	0	37	6·2	450°	200	0	0	90·0	6·7		3·3	0·771	38·5	18·3	39·2	4·0	42·5	38·2	16·5	35·2	27·5	44·3	18·5	
4	28	60	110	224	95	450°	200	11·6	5·8	89·5	14·2		2·1	0·741	46·9	19·7	29·6	3·8	50·7	45·4	17·6	26·5	13·8	19·7	9·9	I
5	36	60	110	222	96	450°	200	11·5	5·8	89·5	13·1	0	3·2	0·746	44·5	19·8	33·5	2·2	46·7	41·8	17·7	30·0	12·8	19·2	9·8	I
0	28	60	0	48	8	450°	200	0	0	87·7	11·0		1·3	0·767	47·9	19·9	28·8	3·4	51·3	45·0	17·4	25·3	(27·4)[2]	39·4	16·8	
0	30	120	110	223	85·5	450°	200	11·6	5·8	78·0	22·2		5·6	0·718	67·8	17·5	10·0	4·7	72·5	56·6	13·7	7·8	12·8	15·3	7·6	I
6	32	60	110	228	85	460°	200	11·6	5·8	77·0	23·7	0	5·1	0·719	69·0	16·9	9·5	4·6	73·6	56·7	13·0	7·3	15·0	17·4	8·3	I
2	25	120	0	68	16	450°	200	0	0	73·0	21·9	0·3	4·8	0·766	65·8	16·6	14·0	3·6	69·4	50·6	12·1	10·2	(23·0)[2]	27·7	11·7	
7[1]	25+27	240	110	260 (220·5)	90·5 (82)	450°	200	15·2	7·6	65·7	35·5	0	6·4	0·703	83·0	9·5	2·5	5·0	88·0	57·8	6·2	1·6	8·8	9·5	5·2	I
1[1]	23+25	240	0	90 (70·2)	24·5 (15·8)	450°	200	0	0	51·5	37·8	4·0	6·7	0·777	71·9	11·3	13·1	3·7	75·6	38·9	5·8	6·7	(17·5)[2]	20·5	10·3	
2	20	60	110	222·5	102	450°	100	12·9	12·9	87·5	20·8		4·6	—	36·3	18·4	43·5	1·8	38·1	33·3	16·1	38·1	—	18·3	10·1	I
3	27	60	110	220	92·5	450°	300	9·7	3·2	93·3	7·7	0	2·2	0·753	36·6	19·7	39·6	4·1	40·7	38·0	18·4	36·9	14·3	22·1	11·3	I

[1] In these experiments the heating was interrupted half way through, the autoclave was cooled (pressures 82 and 15·8 kg. per sq. cm. respectively), hydrogen was added, in the case of experiment 87, to 110 kg. per sq. cm. (none was added 260 and 90 kg. per sq. cm. respectively; 220·5 and 70·2 kg. per sq. cm. had been reached in the first period of heating.

[2] Approximate determinations

[3] CO_2 absent.

Ingoing Material.			Product (per cent. on wax charged).					English			
									Per cent. by w liquid proc		
ax .).	Gas (g.).	Gas (per cent. on wax).	Oil.	Gas.	"Carbon."	Loss (calculated).	Specific gravity.	Gasoline to 220° C.	Kerosene 220°–300° C.	Residue above 300° C.
00	11·4	5·7	99·7	6·1			—	—	—	—
00	12·7	6·3	99·7	6·6			—	2·3	2·4	94·8
00	0	0	99·3	0·7			0·884	2·5	2·9	94·2
00	12·4	6·2	98·5	7·7			—	9·3	8·4	81·7
00	0	0	96·8	2·2	0	1·0	0·831	15·1	12·2	71·4
00	12·7	6·3	94·5	9·2		2·6	0·819	20·3	14·3	64·2
00	0	0	92·5	4·3		3·2	0·781	28·2	16·3	52·8
00	12·7	6·3	94·3	9·2		2·8	0·755	30·6	18·0	48·8
00	0	0	90·0	6·7		3·3	0·771	38·5	18·3	39·2
00	11·6	5·8	89·5	14·2		2·1	0·741	46·9	19·7	29·6
00	11·5	5·8	89·5	13·1	0	3·2	0·746	44·5	19·8	33·5
00	0	0	87·7	11·0		1·3	0·767	47·9	19·9	28·8
00	11·6	5·8	78·0	22·2		5·6	0·718	67·8	17·5	10·0
00	11·6	5·8	77·0	23·7	0	5·1	0·719	69·0	16·9	9·5
00	0	0	73·0	21·9	0·3	4·8	0·766	65·8	16·6	14·0
00	15·2	7·6	65·7	35·5	0	6·4	0·703	83·0	9·5	2·5
00	0	0	51·5	37·8	4·0	6·7	0·777	71·9	11·3	13·1
00	12·9	12·9	87·5	20·8		4·6	—	36·3	18·4	43·5
00	9·7	3·2	93·3	7·7	0	2·2	0·753	36·6	19·7	39·6

y through, the autoclave was cooled (pressures 82 and 15·8 kg. per sq. cm. respectively), hydrogen w
cm. had been reached in the first period of heating.

Analysis of the Liquid Product.										Gas.											
Engler Distillation.							Bromine value (addition).			Gas charged (litres).	Gas obtained (litres)[2].									Hydrogen fixed.	
Per cent. by weight on liquid product.				Per cent. by weight on wax charged.																	
sene 0°– ° C.	Residue above 300° C.	Loss.	Gasoline + loss.	Gasoline + loss.	Kero-sene.	Residue.	Liquid product.	Gasoline.	Kero-sene.	Hydro-gen.	Oxygen.	Total.	Heavy hydro-carbons.	Oxygen.	Carbon mon-oxide.	Hydro-gen.	Other hydro-carbons.	Nitro-gen.	C-atoms (av.) in 'other hydro-carbons.'	In g.	Per cent. on wax charged.
—	—	—	—	—	—	—	—	—	—	105·2	1·4	106·8	—	1·0	0·0	104·5	0·3	0·6	—	—	
·4	94·8	0·5	2·8	2·8	2·4	94·5	4·8	35·1	26·6	109·7	2·0	112·4	0	2·0	0·0	109·0	0·4	1 0	4·4	—	—
·9	94·2	0·4	2·9	2·9	2·9	93·6	7·5	59·2	41·0	0	0	1·0	0·1	0·0	0·0	0·2	0·2	0·4	2·4	—	—
·4	81·7	0·6	9·9	9·7	8 3	80·5	8·2	30·0	16·9	106·9	2·0	104·6	0	0·2	0·4	101·4	1·8	0·8	3·0	0·5	0·3
·2	71·4	1·3	16·4	15·9	11·8	69·1	19·6	57·4	26·0	0	0	3·2	0·6	0·0	0·0	0·3	1·3	0·8	2·3	—	—
·3	64·2	1·2	21·5	20·3	13·5	60·7	12·8	25·0	13·1	109·4	2·0	104·4	0	0·4	0·4	98·8	3·1	1·7	3·0	0·9	0·5
·3	52·8	2·7	30·9	28·6	15·1	48·8	25·1	47·6	20·8	0	0	5·8	1·3	0·0	0·1	0·7	3·9	0·7	2·2	—	—
·0	48·8	2·6	33·2	31·3	17·0	46·0	10·5	23·5	12·3	110·1	2·0	96·5	0·2	0 8	0·1	88·4	3·5	3·5	2·5	1·9	1·0
·3	39·2	4·0	42·5	38·2	16·5	35·2	27·5	44·3	18·5	0	0	10·4	2·4	0·1	0·1	1·0	5·7	1·0	2·2	—	—
·7	29·6	3·8	50·7	45·4	17·6	26·5	13·8	19 7	9·9	113·0	1·0	100·0	0·6	0·8	0·0	87·7	9·1	1·8	2·2	2·3	1·1
·8	33·5	2·2	46·7	41·8	17·7	30·0	12·8	19·2	9·8	112·1	1·0	98·5	0·8	0·4	0·6	87·0	8·4	1·5	2·2	2·2	1·1
·9	28·8	3·4	51·3	45·0	17·4	25·3	(27·4)[2]	39 4	16·8	0	0	18·9	3·5	0·2	0·2	1·9	12·5	0·6	2·1	—	—
·5	10·0	4·7	72·5	56·6	13·7	7·8	12·8	15 3	7·6	113·8	1·0	101·0	1·0	0·4	0·7	77·0	20·4	1·5	2·5	3·3	1·6
·9	9·5	4·6	73·6	56·7	13·0	7·3	15·0	17·4	8·3	113·0	1·0	100·5	1·3	0·6	0·5	75·3	21·2	1·5	2·4	3·4	1·7
·6	14·0	3·6	69·4	50·6	12·1	10·2	(23·0)[2]	27·7	11·7	0	0	32·5	4·3	0·5	0·4	2·3	23·7	1·3	2·2	—	—
·5	2·5	5·0	88·0	57·8	6·2	1·6	8·8	9·5	5·2	142·0	1·7	116·4	1·4	0·9	0·8	76·2	35·4	1·7	2·5	5·9	2·9
·3	13·1	3·7	75·6	38·9	5·8	6·7	(17·5)[2]	20·5	10·3	0	0	55·6	3·2	0·4	0·4	3·4	47·8	0·4	2·1	—	—
·4	43·5	1·8	38·1	33·3	16·1	38·1	—	18·3	10·1	126·4	1·1	115·5	0·6	0·8	0·5	107·5	4·7	1·4	2·1	1·7	1·7
·7	39·6	4·1	40·7	38·0	18·4	36·9	14·3	22·1	11·3	103·1	0·3	86·5	0·9	0·5	0·3	74·5	7·8	2·4	2·4	2·6	0·9

), hydrogen was added, in the case of experiment 87, to 110 kg. per sq. cm. (none was added in the case of experiment 94) and the heating resumed. The maximum pressures then attained were

EXPERIMENT No. XXII.

Before the experiment.	Gr.	After the experiment.	Gr.
In cottonseed oil	21·7		
		In gases * CO_2, CO, O_2 ..	16·3
In supplied hydrogen (O_2 content 2·5%) ..	3·9	In water	7·5
Total ..	25·6	Total ..	23·8

EXPERIMENT No. XXV.

Before the experiment.	Gr.	After the experiment.	Gr.
In cottonseed oil	21·5		
		In gases * CO_2, CO, O_2 ..	15·7
		In water	3·1
		Total ..	18 8

* Leaving water vapour out of consideration.

In those experiments where the oil was heated in the presence of hydrogen under high pressure, less coke and residue and more gasoline was obtained. The gasoline and the kerosene from the experiments without addition of hydrogen were more unsaturated than the corresponding products obtained after the same time of heating in the presence of hydrogen.

At this high temperature we have to deal with a rapid transformation of fats into hydrocarbons. The great velocity of this transformation is seen particularly from experiment XXVII. Here the time to reach the reaction temperature was 36 minutes, and, although 450° C. was applied for only 5 minutes, an important part of the oxygen has been expelled.

In considering hydrogenation in the petroleum industry, it is clear that we have to expect less, in the technical sense, from processes which demand the addition of a catalyst. It may be expected that a catalyst such as nickel will soon be poisoned by the products which are found in crude oil, or distillates, or in residues.[10] Without a catalyst, even at very high pressure, the probability of hydrogenation with sufficient velocity is slight. An example is the negative result already mentioned with the cotton-seed oil at 180° C., without a catalyst in the presence of hydrogen at high pressure.

That a direct hydrogenation of unsaturated hydrocarbons is strictly needed in the petroleum industry must be denied, for the properties of different oil-distillates, even if a greater or smaller percentage is unsaturated, are sufficient for most technical applications.

In commercial trade there are several brands of gasoline that satisfy the conditions, notwithstanding that their bromine value

[10] F. Bergius, Neue Methoden zur Verarbeitung von Mineralöl und Kohle, *Z. f. angew. Chemie*, 1921, **34**, 342.

(addition) indicates an important unsaturation. As an example of this we give the bromine values of three of the most important Dutch kinds of gasoline (August, 1924):—

Bromine value (method of McIlhiney).		
A.	B.	C.
7·5—9·3 ..	3·8—4·1 ..	0·7—2·3

It is clear that this unsaturation must be of a good nature and must not cause the gumming of the products when exposed to light. The samples mentioned, when exposed to the light of a quartz burner, however, proved not to be quite stable. A, after 34 hours, had become pale yellow; B, after the same duration, remained quite uncoloured. The bromine value of A after this experiment had not altered much (6·4–8·3).

The available quantities of products, such as naphthalin, which may be used as raw material for the hydrogenation to tetralin or to decalin[11] are but small compared with the available quantities of coal, crude oils and distillates. Therefore, naphthalin cannot be an important raw material for the production of liquid fuels.

Generally very high temperature will not be advantageous for direct hydrogenation of special unsaturated hydrocarbons in the absence of a catalyst. It may be expected that a loss of hydrogen occurs at very high temperature rather than hydrogenation. The formation of cyclic saturated hydrocarbons, such as cyclohexane (and derivatives) from benzene, etc., and hydrogen at temperatures exceeding 250°—300° C. becomes very small, and just the opposite reaction (the dehydrogenation) with the evolution of hydrogen becomes important[12]; this holds for the presence of catalysts like nickel.

Hydrogen under very high pressure will be able to obstruct to some degree the reactions of dehydrogenation of the hydrocarbons.

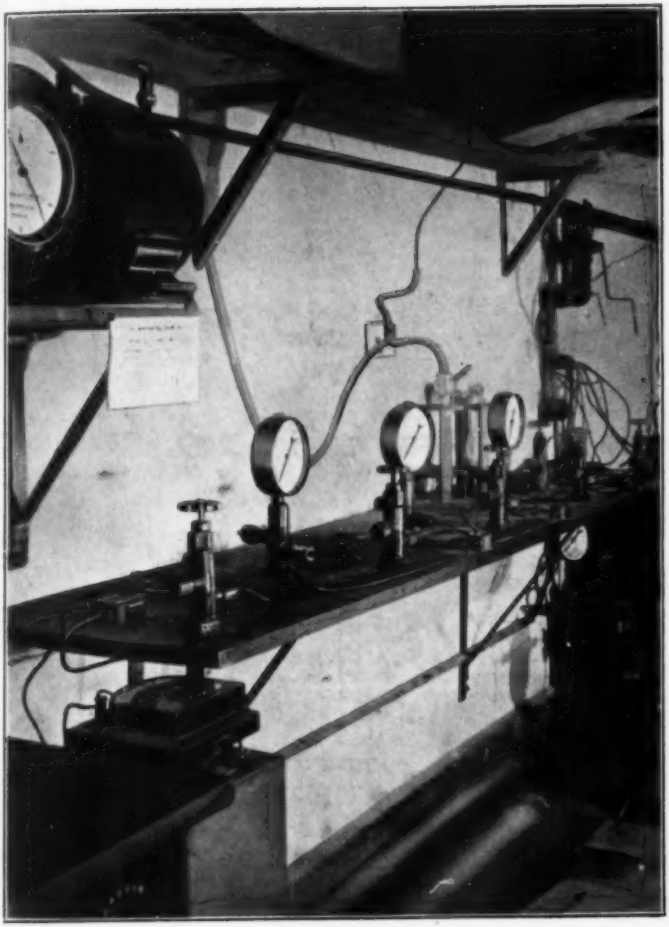
In the petroleum industry hydrogenation is not the most important thing, but still more essential is to obtain in "cracking" a yield as high as possible of low-boiling distillates (gasoline). High yields are obtained in different methods of cracking, such as the Dubbs and the Burton processes, but these methods always give residues, especially coke, which gives much trouble. This formation of coke is quite normal in cracking.

Sabatier[13] says:—"L'action d'une température élevée sur les hydrocarbures a pour effet de dissocier leurs molécules, d'où

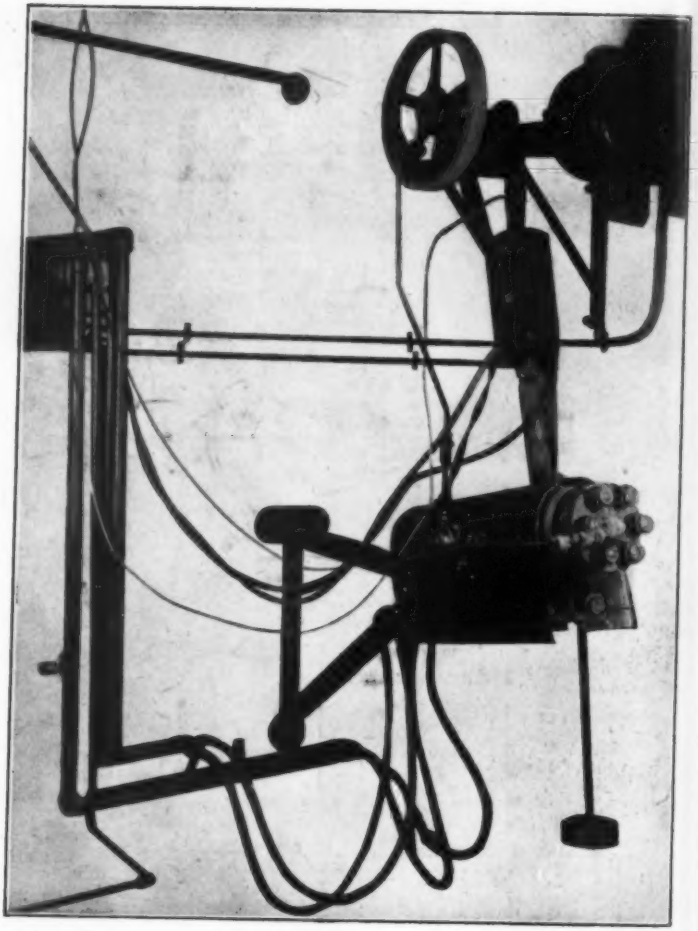
[11] See W. Schrauth, Über die technische Herstellung und Verwendung hydrierter organischer Verbindungen, *Z. f. angew. Chemie*, 1922, **35**, 25; Ch. Lormand, Les hydrures de naphtaline et leur emploi, *Chimie et Industrie, Numéro spécial*, May, 1923, p. 602.

[12] P. Sabatier, La catalyse en chimie organique, 2me Ed., Paris, 1920, pp. 172, 246.

[13] *Loc cit.*, p. 361.



AUTOCLAVE PRESSURE GAUGES, ETC.



AUTOCLAVE, SHOWING ROCKING APPARATUS.

l'hydrogène tend à se séparer, en même temps qu'il se produit un émiettement plus ou moins important en groupes CH_3, CH_2, CH capables de s'unir a l'etat naissant en fournissant de nouvelles molécules complexes. Il en résulte des mélanges compliqués de constitution variée, que Berthelot avait désigné sous le nom d'équilibres pyrogénés, et qui, au fur et à mesure que la température s'éleve, conduisent à des proportions croissantes d'hydrogène et de méthane, en même temps qu'à des matières très riches en carbone et des hydrocarbures très condensés."

It is now of highest importance to exert influence on the reactions of cracking in such a way that, as Bergius[14] says :—"Man dafür sorgt, dasz bei der Spaltung ein Verlust von Wasserstoff nicht eintritt. Wenn das gelänge, müszte es möglich sein, die Ole ohne Koksabscheidung und vollständig in leichtere Produkte umzuwandeln."

Although the Bergius process is frequently considered as a process of hydrogenation, yet we do not have here a pure hydrogenation. It regards more[15] :—1st, the moderation of cracking reactions by high hydrogen-pressure. 2nd, the prevention of polymerisation and of coke-formation from the unstable molecule-fragments obtained at the cracking. Therefore, these molecule-fragments must be hydrogenated.

From this it follows that the fractions which will be obtained in Berginisation will be more saturated.

In Berginisation we have always to deal with temperatures at which most of the hydrocarbons are no more stable (with the exception of methane).

The Berginisation of oxygen-containing bodies, such as coals, will be discussed in a separate paper.

We have proved that the theoretical considerations of Bergius are substantially correct. From our investigations[16] it follows that (*a*) very *high hydrogen pressure is necessary* (initial pressure, 100–110 KG/cM²) ; (*b*) *nascent hydrogen* in Berginisation of paraffin wax has *no advantage*. The experiments with paraffin wax did not give any difference between hydrogen under low-pressure and hydrogen formed by the reaction $CO+H_2O \longrightarrow CO_2+H_2$; (*c*) high pressure of an indifferent gas, such as nitrogen and technical methane does not give such favourable results as are obtained with hydrogen at high pressure ; (*d*) the heating in a closed autoclave, or the heating in one which has been filled before with a little hydrogen, methane or nitrogen under high pressure or with CO ($+H_2O$), and by which pressures of 50 atmospheres and higher

[14] *Loc. cit.*, p. 342.
[15] F. Bergius, *loc cit.*, p. 345.
[16] *J. Inst. Petr. Tech.*, 1924, **10**, 45, p. 670.

were reached during the heating, is consequently better than a heating by which one keeps the pressure constant at 7 atmospheres and distils in the meantime. The favourable results are apparent from the higher yields of oil (and therefore lower production of gas); besides the gas contains less heavy hydrocarbons, while the oil is less unsaturated.

II.

Decomposition of Paraffin Wax at 450° C. in Presence and in Absence of Hydrogen under High Pressure.

Earlier investigations have shown the favourable influence of hydrogen under high pressure on the process of decomposition which occurs when paraffin wax is heated to 450° C. It was found that hydrogen under high pressure:

(a) Enters into combination, and forms part of the products, during the reactions which are proceeding.
(b) Causes the production of less unsaturated distillates (gasoline and kerosene).
(c) Lowers the specific gravity of the residue obtained on distillation of the reaction-product.

Notwithstanding the lack of experimental data and our imperfect knowledge of the reactions which occur, we have been successful in adding to our knowledge of the Berginisation process. We have reached this result by studying the influence of time on the decomposition at 450° C. of paraffin wax in the presence and in the absence of hydrogen under high pressure. The raw material which was used in these experiments was Rangoon paraffin, solidifying point (Shukoff) 58°, specific gravity 20°/4°: 0·913. Elementary analysis gave 84·6 per cent. C. and 14·8 per cent. H. The charge for each experiment was 200 grams; this was heated at 450° C. in the autoclave already described by us.[17] To promote mixing, three steel balls of a total weight of 79·5 grams were added. The chief results are shown in the appended table.

The Influence of Time on the Decomposition of Paraffin Wax at 450° C. Without the Addition of Hydrogen ("Cracking.")

The quantity of gas produced and the maximum pressure reached increase with time of heating; the pressure after cooling and the volume of gas obtained likewise increase. The volume of "heavy

[17] Journal of the Institution of Petroleum Technologists, Vol. 10, No. 45, September, 1924, pp. 671—672; Proceedings Koninklijke Akademie van Wetenschappen, Amsterdam. xxvii. (1923-24) p. 83.

hydrocarbons" also increases to a determined limit and in experiment 92 this maximum is reached. The quantity of hydrogen liberated increases regularly, while the average number of atoms of carbon per molecule of the methane hydrocarbons obtained

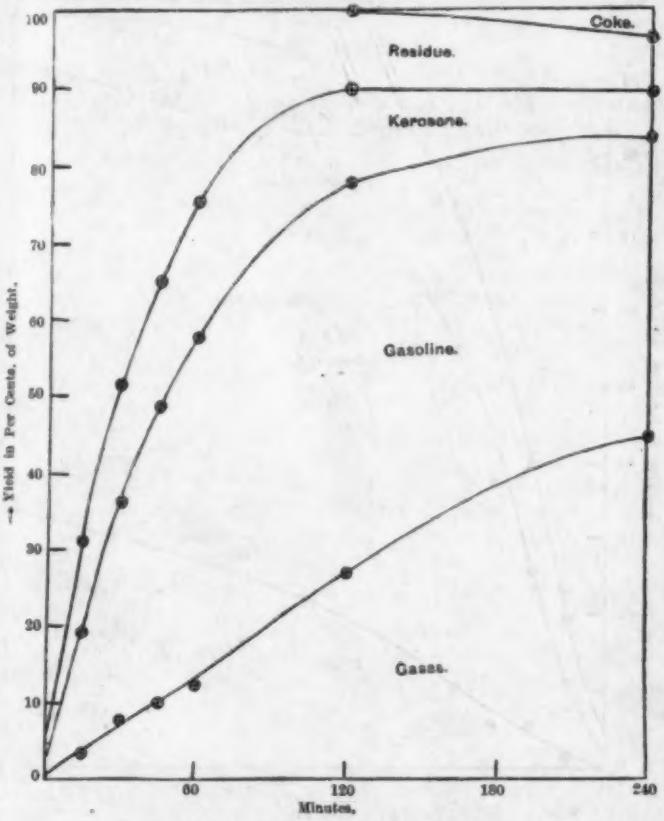


FIG. 1.

"Cracking" (450° C.) of Paraffin Wax. Yield in Per Cents. of Weight.

does not show much variation; it decreases from 2·4 to 2·1. Only traces of coke are formed at first. After two hours (experiment 92) 0·3 per cent. of "carbon" is found; but, after 4 hours, this has increased to 4·0 per cent. in the case of experiment 94. Our experiments indicate that the process is a normal one; the paraffin

hydrocarbons break down, immediately forming decomposition products such as the lower hydrocarbons (ethane and probably methane), and hydrogen. Since the liberation of "carbon" is not immediate, but takes place subsequently with great rapidity,

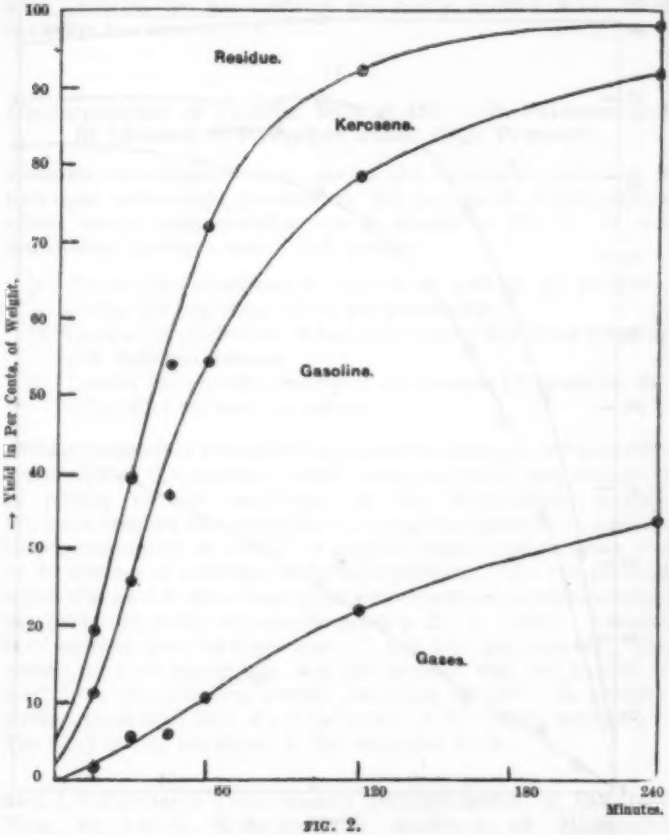


FIG. 2.

"Berginisation" (450°) of Paraffin Yield in Per Cents. of Weight.

it must do so at the expense of the products of decomposition, and not of the hydrocarbons present in the unaltered paraffin wax itself. The oil produced by short periods of heating solidifies completely at ordinary temperatures, while with longer periods the product becomes more liquid, notwithstanding the formation of considerable quantities of gas. At first the specific gravity

diminishes rapidly, until after about one hour's heating the minimum is reached (No. 89, 0·767; No. 92, 0·766). Thereafter the liberation of "carbon" begins and at the same time the specific gravity of the oil rises (No. 94, 0·777).

The liquid product becomes progressively richer in gasoline although the absolute yield of gasoline (Fig. 1) after a rapid initial increase diminishes after two hours (after 2 hours, 50·6 per cent.; after 4 hours, 38·9 per cent.). The percentage of kerosene in the liquid product diminishes after the first hour, as does the percentage yield (Fig. 1.). The quantity of residue boiling above 300° C. diminishes continuously with the percentage yield (Fig. 1). These facts show that at first gas, gasoline and kerosene increase at the expense of the residue, but that subsequently the kerosene and gasoline at first formed diminish with the residue. As a result it is only the yield of gas which increases, with accompanying liberation of "carbon." It must be understood that none of the fractions mentioned remains unaltered during the process. The whole system, excluding such constituents as hydrogen and methane, is in a condition of continual decomposition. This is proved by the decrease in the bromine values of the oil produced (7·5, 19·6, 25·1, 27·5, 27·4, 23·0, and 17·5 after 1, 15, 30, 45, 60, 120 and 240 minutes respectively). This decrease occurs after a preliminary increase (Fig. 3). The quantity of heavy hydrocarbons in the gas at first rises, but after two hours begins to fall, with an accompanying decline in the bromine value. The lowering of the bromine value is probably not due to the formation of gaseous unsaturated products such as ethylene, but rather to the occurrence of polymerisation. In this connection it is interesting to note that the specific gravity of the residue from the oil produced by cracking decreases at first, and afterwards increases rapidly, finally becoming greater than unity (Fig. 4). It has already been mentioned that the specific gravity of the liquid product of the cracking experiments rises with prolonged treatment (Fig. 4).

The Influence of Time on the Decomposition at 450° C. of Paraffin Wax in the Presence of Hydrogen under High Pressure (Bergius Process).

In these experiments the autoclave was charged with hydrogen to 110 kg. per sq. cm. before heating. The maximum pressures reached indicate a course of events different from that obtained in the cracking experiments. The maximum pressures 210·5 and 218 kg. per sq. cm. in experiments 99 and 106 are apparently caused merely by the rise in temperature, for decomposition and liberation of gas have hardly begun. Experiments 103, 104, 102, 74, 76 and 80 after 15, 30, 45, 60, 60 and 120 minutes respectively, notwithstanding the decomposition which is taking place, give

maximum pressures which are scarcely higher than those in experiments 99 and 106. This is doubtless because the effect of hydrogenation is becoming important. Confirmation is provided by the observed final pressures, which are smaller in proportion to the duration of the experiment. From the volume and composition of the gas obtained it follows that in experiments 103, 104, 102, 74, 76 and 80, and in 87 (where hydrogen was added twice), 0·3, 0·5, 1·0, 1·2, 1·1, 1·6 and 2·9 per cent. by weight of hydrogen respectively (calculated on the paraffin wax) are fixed.

The bromine values of the original oil produced and of the corresponding gasoline and kerosene (Fig. 3) show that the bromine

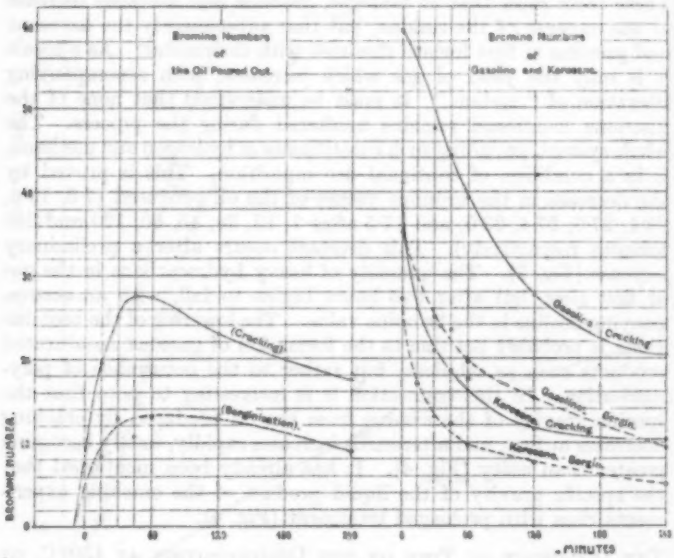
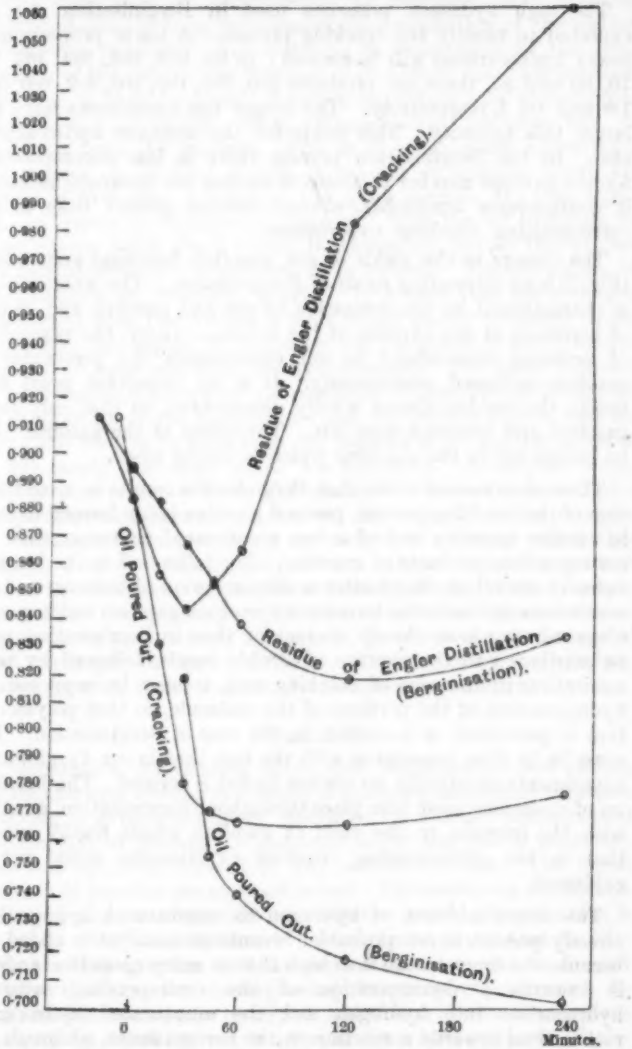


FIG. 3.

value is always lower than in the corresponding cracking experiments. A point of even greater importance is that after 60 and up to 120 minutes' Berginisation there is no decrease in the bromine value of the oil produced, as there is in the analogous cracking experiments. From this it may be concluded that probably polymerisation does not occur in these Berginisation experiments. It is only after further heating that the bromine value of the oil diminishes. Fig. 4 shows that after 120 minutes the specific gravity of the Engler distillation residue increases; up to 120 minutes' Berginisation this specific gravity diminishes.



Specific Weight (120° C.) *of the Oil poured out and of the Residue of Engler Distillation.*

FIG. 4.

The high hydrogen pressures used in Berginisation may be expected to modify the cracking process. A lower proportion of heavy hydrocarbons will be formed; in 99, 106, 103, 104, 102, 74, 76, 80 and 87, there are produced 0·0, 0·0, 0·0, 0·0, 0·2, 0·6, 0·8, 1·0 and 1·4 l. respectively. The longer the experiment lasts, the larger this quantity. This holds for the methane hydrocarbons also. In the Berginisation process there is less decomposition, for the average number of atoms of carbon per molecule, although it continuously diminishes, always remains greater than in the corresponding cracking experiments.

The change in the yields of gas, gasoline, kerosene and residue (Fig. 2) is an interesting result of Berginisation. The whole process is characterised by the formation of gas and gasoline and at first of kerosene, at the expense of the residue. Later, the percentage of kerosene diminishes. In our experiments the percentage of gasoline increased continuously. It is an important point that finally the residue almost wholly disappeared, so that only gases, gasoline and kerosene were left. The origin of the gasoline must be looked for in the cracking which is taking place.

These observations show that Berginisation results in a modification of the cracking process, gas and gasoline being formed initially in smaller quantity and of a less unsaturated character than the corresponding products of cracking. The falling off in the bromine value of the oil produced after a certain period of heating, and the continuous decline in the bromine value of the gasoline and kerosene, observed even more clearly in cracking than in Berginisation, must be attributed to the rupture of double bonds, followed by polymerisation in the case of cracking and, it may be supposed, by hydrogenation of the portions of the molecule, so that polymerisation is prevented or modified, in the case of Berginisation. This must be in close connection with the fact that in our Berginisation experiments practically no carbon (coke) is formed. The breaking up of molecules must take place throughout Berginisation, as otherwise the increase in the yield of gasoline, which finally exceeds that in the corresponding cracking experiments, could not be explained.

The direct addition of hydrogen to unsaturated hydrocarbons already present is not probable, because no catalyst is added and because the temperature is so high that in many cases the tendency is towards a decomposition of the corresponding saturated hydrocarbon into hydrogen and the unsaturated hydrocarbon rather than towards a reaction in the reverse sense, although this decomposition will be modified by the presence of hydrogen under high pressure. We hope to deal with this subject in more detail at a later date.

The advantage of Berginisation as compared with cracking appears distinctly from the elementary composition of the residue in the two processes. For instance, in experiment 87 the composition of the residue was 85·4 per cent. carbon and 13·8 per cent. hydrogen, in 94 91·8 per cent. of carbon and 8·2 per cent. of hydrogen, respectively; in other words, Berginisation prevents loss of hydrogen from the residues. This is of considerable importance, the process of cracking always giving oils or residues which are poorer in hydrogen, because in the gases formed, H_2, CH_4, C_2H_6, etc., an excess of hydrogen is present. This loss of hydrogen to some extent takes place during Berginisation, but in this process the loss of hydrogen is supplied from outside. The advantage of Berginisation is, therefore, proved. It is true that the hydrogen introduced from the outside is later found wholly or partly in the gases, but this supply of hydrogen has prevented a too extensive removal of hydrogen from the hydrocarbons. The great influence of temperature is shown by a comparison of experiments 78 and 80. In experiment 78 the temperature was ten degrees higher, and the effect was that in half the time (60 minutes in 78 and 120 minutes in 80) nearly the same result was obtained. Analogous observations were made by Dr. A. E. Dunstan.[18] The ten degrees higher temperature has apparently doubled the velocity of the complex of reactions. This fact being mentioned it must be added that without a more detailed study of this subject there is not much matter for discussion on the theoretical significance of this observation. That the quantity of paraffin wax used has a great influence appears from experiments 72 and 68, in which the percentage of fixed hydrogen is quite different. It is necessary, therefore, always to work under completely comparable conditions.

Summary.

Comparative experiments show that Berginisation has various advantages over heating in absence of hydrogen under high pressures (cracking). After some hours' Berginisation a larger percentage of gasoline and of kerosene is obtained, while less gas is produced. Coke has not been formed to any material extent. The liquid products of reaction are more saturated. The residue on distillation (boiling point exceeding 300° C.) after 4 hours' Berginisation is but small. On the other hand, it must be observed that in Berginisation less gasoline and correspondingly less gas is formed initially than in the corresponding cracking experiments. In Berginisation cracking is restricted and the very reactive residues produced by cracking are converted into hydrocarbons of the gasoline and kerosene distillates. Polymerisation and the formation

[18] *Journ. Inst. of Petrol. Technol.* (1924.)

of coke from the unsaturated residues is thus prevented or diminished.

While cracking gives rise to residue poor in hydrogen, Berginisation prevents the loss of hydrogen from residues. In one Berginisation experiment a residue was obtained which gave 13·8 per cent. of hydrogen, whereas the raw material contained 14·8 per cent. In a corresponding cracking experiment the residue contained only 8·2 per cent. of hydrogen.

Berginisation must be considered as a combined cracking and hydrogenation process. The useful feature of cracking, the breaking down of hydrocarbon molecules, remains, but is made more regular, while the products are obtained in a more stable condition on account of the addition of hydrogen, so that extensive polymerisation and formation of coke are avoided. The main feature of Berginisation, is, therefore, not the saturation of unsaturated hydrocarbons already present. In this respect it differs widely from the ordinary hydrogenation of vegetable or animal oils, which is conducted in the presence of catalysts.

This investigation clears up the scientific significance of the *Bergius* hydrogenation process.

In continuation of this research the isolation, as far as possible, of the chemical compounds formed will be attempted, while our results on the hydrogenation of coal by the *Bergius* method will be published shortly.

We wish to express our thanks to Mr. A. C. Ouborg, who assisted us during the course of these investigations.

Nature of the Product and of the Distillation Residue.

Experiment.	Minutes heating after the reaction temperature has been reached.	Product.	Residue.
106	1	Spw	Spw
107	*1*	*Spw*	*Spw*
103	15	Spw	Spw
108	*15*	*Spw*	*Spw*
104	30	Spw	Spw
109	*30*	*Sv*	*Sv*
102	45	Spw	Spw
111	*45*	*L (dark)*	*Sv*
74	60	Spw	Spw
89	*60*	*L (dark)*	*Sv*
80	120	L (clear)	Spw
78	60 (temp. 460°)	L (clear)	Spw
92	*120*	*L (dark)*	*L (dark)*
87	240	L (clear)	L (dark)
94	*240*	*L (dark)*	*L (dark)*

Spw—solid, like paraffin wax. Sv—consistency of vaseline.
L (dark)—liquid, dark. L (clear)—liquid, clear.

DISCUSSION.

The Chairman (Dr. A. E. Dunstan), in opening the discussion, said it would be agreed that the members had listened to a paper of consummate importance, and one which had been presented to them in a delightfully clear, concise and interesting way. Prof. Waterman visualised hydrogenation with the detached air of a man of science, but speaking as a practical chemist, he (the Chairman) could see no particular reason to alter the views which he had put forward before the Institution on a number of occasions, namely, that so far, at any rate, as mineral oil was concerned, he did not see at the moment how Berginisation was going to offer any greater inducements than straight cracking. In the diagrams which had been shown on the screen, it was unfortunate that the experiments in which no hydrogen was used had had no other means for production of pressure; and he would like to ask Prof. Waterman whether if he actually added a second component—nitrogen, carbon dioxide, methane or so forth—and had the same initial pressure as with hydrogen, what effect he would then find; because in some work which he himself and his colleagues had carried out some time ago they had been interested to notice that when they had used similar initial pressures of nitrogen, hydrogen, steam, carbon dioxide and so forth, the product after the cracking, or the hydrogenation, or whatever it was, had yielded almost identical figures on ultimate analysis. To take two cases, in an experiment using nitrogen the product had 12·5 per cent. hydrogen and 86·5 per cent. carbon, and the corresponding experiment with hydrogen gave 12·4 per cent. hydrogen and 86·3 per cent. carbon; the figures were identical, within the ordinary limit of experimental error.

Looking at the tables at the end of the paper there were one or two things which he considered were well worth investigation. If one looked, for example, at experiments 103 and 108, then in the hydrogenation experiment starting with 110 atmospheres pressure, and carrying on the experiment for 15 minutes, the gasoline yield was 9·7 per cent. In the corresponding cracking experiment, with no hydrogen added and for the same period of time, the same temperature and so on, the gasoline yield was 15·9 per cent. That 15 minutes was roughly about the time to which the material was exposed to conditions of temperature and pressure in many of the technical cracking operations, and there was a clear advantage of 6 per cent. gasoline yield in the cracking operation. Then, looking at experiments 102 and 111, one found the ratios 31·3 per cent. and 38·2 per cent. of gasoline after 45 minutes; and towards the end after four hours (which would be a time

unthought of in technical cracking) one got the ratio 57·8 per cent., 38·9 per cent. in favour of the Berginisation experiment. He would like to see corresponding experiments in which hydrogen, nitrogen, carbon dioxide, etc., were used as pressure producing means.

In the case of Rangoon wax he noticed the ultimate analysis added up to 99·4 per cent. He would like to ask Prof. Waterman if he thought the missing 0·6 per cent. was oxygen.

In connection with Fig. I it would be noticed that one only got carbon in cracking operations after two hours' heating. That was very significant. Personally he agreed with Prof. Waterman that the formation of carbon was secondary or even tertiary, due to some subsequent reactions entirely removed from the actual cracking operation itself and that if one could remove the bodies which formed the coke before further decomposition occurred, it would be a tremendous advantage in the technology of cracking.

A statement was made that the specific gravity diminished rapidly during cracking. He would like to mention one observation which he and his colleagues had made in their experiments, viz., that if one took crude gas oil and cracked it, immediately after the cracking temperature was reached there was always observed a slight increase in gravity. Later on, of course, one got a falling off in gravity. He wondered how far Prof. Waterman's results were taken in point of time from the actual occurrence of cracking.

Prof. Waterman also pointed out that an increase of 10° C. doubled the rate of reaction. In this and his colleague's recent paper on cracking* some months ago they had made the same observation. It did rather look as though this was one further illustration of that very remarkable natural law, that an increase of 10° C. doubled the rate of reaction in quite a number of cases.

Prof. Brame said that he was particularly interested in the point which Dr. Dunstan had raised, namely, the question of obtaining pressure by other gases. There was, of course, the question of mass action which came in, but probably only to a slight extent. The members knew, for instance, the usual effect of increasing the concentration on the one side, and, as one would expect, if one increased the hydrogen to a very considerable extent, that decomposition of hydrocarbons which tended to throw off hydrogen would in some considerable measure be restricted. There was also the question of the effect of pressure in the same direction. Prof. Waterman did mention, and showed a table of results obtained with cotton-seed oil, using nitrogen, carbon monoxide, methane and other gases.

* Recent Development in the Art of Cracking, A. E. Dunstan and Robert Pitkethly. *Journ. Inst. Petr. Techn.* **X**, 146, 28, 1924.

There were some very striking figures in the paper where the product in the one case contained 13·8 per cent. of hydrogen and in the other case only 8·2. He was rather in agreement with Dr. Dunstan on the question of the possible commercial value of the Berginisation process as applicable to mineral oils. The question was, was it worth while? Was any possible development of Berginisation applied to mineral oils likely to compare on a commercial scale with cracking plants, from the point of view of possible throughput and the cost of the plant? One would not pursue that argument with regard to other materials.

The table at the end of the paper was of very great interest. The amount of material which had been worked on by Prof. Waterman and his colleague had been small. The wax had been of the order of a couple of hundred grammes, and therefore the yield of product had not been sufficiently great for that investigation which he thought was very desirable, namely, as to the nature of the liquid products. They had boiling ranges, and bromine values, but he thought it would be particularly interesting to know whether there was any material production of aromatic or other cyclic hydrocarbons, because that might throw light on the general changes—whether polymerisation and so on were being obtained. It was, however, striking that when one came to the long period experiments, the specific gravity of the products was very low, in experiments Nos. 80 and 78 0·718 and 0·719 respectively, whereas in the absence of the hydrogen the plain cracking gave a gravity of 0·766. It certainly suggested that the hydrocarbons there were paraffins, in the main.

He must say that he felt a certain amount of scepticism about some of the gas analyses. In a mixture containing a very high proportion of hydrogen, it was a matter of difficulty to determine hydrocarbons with any degree of exactitude, and in many cases in the paper hydrogen so preponderated that the "heavy hydrocarbons" and "other hydrocarbons" were present in very small amounts. He should prefer some other expression for the "heavy hydrocarbons" and "other hydrocarbons"; they seemed to him rather indefinite.

Dr. V. Henny said that, in view of the time-limit set by the President, he could not fully express his appreciation of the work done by Professor Waterman. He desired to make a remark on one point of the experiments, a point which Professor Brame had also mentioned, *i.e.*, that 200 grammes of paraffin wax has been used throughout the tests. His contention was that by varying the quantity of the paraffin wax, different quantities of gasoline would be obtained. If one started with just one gramme and finished with a quantity which filled the autoclave completely

the yields of gasoline would be from zero to maximum and zero again. His contention was that by using hydrogen one simply displaced that maximum but one did not raise it, and that therefore by increasing the amount of wax in the apparatus a point would be reached where one equalled the yield of gasoline obtained by using hydrogen; and therefore he did think that hydrogen or nitrogen would give finally the same results.

Regarding the commercial value of Berginisation, Dr. Henny said he could not share Prof. Waterman's view that Berginisation had at present any very great advantages over cracking, and quoted in support of his statement French and German opinions unfavourable to its commercial value.

The French opinion was the report drawn up on the Budget of the French Ministry of Public Works which summarises as follows :—" The difficulty of the problem at the present time is not to manufacture a few decilitres of petroleum, but to obtain the industrial realisation of the different processes, and this is not at present realised either in France or abroad."

The German opinion was derived from the lately published balance-sheet of the Erdöl und Kohle-Verwertung A.-G. of Berlin which did not mention one single commercially operating Berginisation plant, and a statement in the same balance-sheet that the Bataafsche Petroleum Mj., one of the most important producing companies of the Royal Dutch Shell, entered into an agreement with the Erdöl und Kohle-Verwertung A.-G. in 1920.

Notwithstanding five years of investigations, the Royal Dutch Shell Group does not operate one commercial Berginisation plant, on the contrary, in the last couple of years, cracking has been developed very considerably by the companies of this Group.

Dr. W. R. Ormandy said that Prof. Waterman had carried out a series of experiments—probably the first which had been published—dealing with, as nearly as may be, a constant material of fixed composition, varying as far as could be, one variable at a time.

He did not think Prof. Waterman was quite justified in drawing the conclusions which he had from the results, but he had brought out a considerable number of facts which previously were not known. He thought it was very unfortunate that Prof. Waterman did not carry out some experiments with nitrogen under pressure corresponding to the pressures used with hydrogen. Those experiments, however, had been made in the Bergius laboratory, and it was to be hoped that at an early date Prof. Waterman would give the Institution the records of a series of experiments carried out with nitrogen and with hydrogen under similar conditions of temperature, time and pressure.

What was of very great interest was the fact that Prof. Waterman found that the amount of hydrogen which had disappeared was of the order varying from 1 to 2·8 per cent., according to time, and that in actual fact the amount of hydrogen that was found to disappear in Berginising some 5,000 tons of mineral oil was from 1·9 to 2·1 per cent.

A great deal was frequently made of the fact that cracked oils contained a lot of unsaturates; that they contained sulphur compounds and so on. As a matter of fact from quite a large number of the commercial cracking plants in use to-day it was possible to take the oil straight from the cracking plant with a very slight refining and to use it without any detriment whatsoever in the motor-car. It was a question entirely of the length of time that the petrol had to be stored before use. He did not think the presence of very considerable quantities of unsaturateds could be held to condemn petrol for use in the modern motor-car. They had yet to distinguish between that type of unsaturated which would cause gumming, and that type which was valuable; just as in lubricating oil certain types of unsaturated led to an improved lubricating oil and if one removed all the unsaturated it left one with paraffinum-liquidum, which was very good for lubricating one's internal anatomy under certain conditions, and only that.

A very interesting point was raised in the early part of the paper, dealing with vegetable oils. Apparently when vegetable oils were heated in the absence of hydrogen complex pyrogenetic changes took place. In the presence of hydrogen, however, the oxygen came off with a carbon or hydrogen atom to which it was apparently connected in the compound itself, and hydrogen probably came in to stop the gap, the place where the carbon was broken off. It had been proved by Bergius that in the hydrogenation of brown coals and lignites containing very considerable amounts of oxygen large amounts of CO_2, CO and H_2O were given off, and that the consumption of hydrogen was very little more in dealing with lignites containing very considerable quantities of oxygen than with the Berginisation of coal containing very small amounts of oxygen.

With regard to the nature of the products which were formed during Berginisation of the wax, of that he was ignorant; and he thought Prof. Waterman was going to have a very difficult problem if he was going to collect enough volatile products from 200-gramme charges to enable him to make a real investigation of the nature of the low boiling-point bodies which were formed. In his own laboratory they had been working for some months on three litres of those light products obtained from the Berginisation of coal, and they had succeeded in proving that the paraffins were approximately 30 per cent.; that the aromatics were about 18 per cent., and that the rest were naphthenes. The paraffins,

strangely enough, were chiefly in the very low boiling point fractions and consisted chiefly of pentane and isopentane. Benzine was there, and toluene. They had succeeded in isolating hexa hydrobenzine.

What they were going to do in the direction of trying to isolate the naphthenes, he did not know. He was hoping that some other member would give a method for distinguishing the naphthenes.

He would like to ask whether any member of the Institution had done any work on the conversion of the hydro-aromatics back again into the aromatics by any of the catalytic processes. It might be of interest and of value to pass some of those low boiling-point fractions over a catalysis in such a way as to convert the hydro-aromatics back again to aromatics, when one could distinguish them much more easily. That information would be of very great value.

Mr. H. G. Shatwell said the paper contained a tremendous amount of detail. It was a complete account of the great deal of work which must have been done in its compilation. He would like to congratulate the authors on the valuable researches they were undertaking and on the important nature of their results.

As most of the members knew, they in Birmingham had been experimenting with Berginisation. They had not yet dealt with paraffin wax, though it was on their programme to do so. The results obtained by Berginising and heating a gas-oil, under pressure with nitrogen, agreed very substantially with the results which had been given that evening. For instance, in the Berginisation of gas oil, it had been found that the gases which were evolved contained only very small traces of unsaturateds, whereas in the cracking experiments, they were somewhat considerable—of the order of 3 or 4 per cent.; also when hydrogen was used, the iodine values of the products were lower and no carbon was deposited.

On these three points, therefore, the results at Birmingham agreed with the results obtained by Prof. Waterman and Mr. Perquin. The adoption of bromine or iodine values to indicate the unsaturated nature of the products is in agreement with our practice. The value of a liquid fuel does not depend so much upon its high content of hydrogen as upon the absence of highly reactive unsaturated linkages. Thus a liquid which contains a low percentage of hydrogen may be stable to bromine and therefore be a valuable fuel owing to the ring structure of the contained hydrocarbons. Consequently it might be of considerable interest to investigate the effect of elevated temperatures and extremely high pressures upon straight-chain hydrocarbons in the way of bending a molecule into a ring. If such a reaction

were possible, the use of hydrogen would be unnecessary and a cheaper process might be devised. In this connection, he would like to know whether the bromine values given in the paper are percentages by weight of bromine absorbed and whether the authors consider that bromine values are more reliable than iodine numbers. Further, in these discussions on Berginisation, he thought that sufficient credit was not given to Bergius for the great amount of work which he had done. Not only had he evolved a process which was almost perfect in principle and in detail, but he was continually introducing novelties to reduce still further the costs of operation. Of these, the recovery of hydrogen was not the least important. A recent patent had been taken up in which the residual gases from Berginisation were scrubbed under high pressures with solvents, so that the proportion of hydrogen was considerably increased. Many of these improvements were highly ingenious.

He would also await with interest the publication of Prof. Waterman's work on coal hydrogenation. At Birmingham, six different types of coal had been dealt with, and with one exception, namely, fusain, substantial yields of liquid had been secured. Since the last meeting of this Institution, 60 per cent. of a Lancashire coal had been liquefied, and when it is considered that the plant used did not allow of continuous operation, the results were satisfactory. Similar experiments, in which nitrogen was used instead of hydrogen, invariably failed to lead to the production of even traces of liquid substances, so that the Birmingham experiments have established, beyond all doubt, the feasibility of Berginising coal. Since Prof. Waterman has proved the applicability of the process to oil, the claims of Bergius have been fully proved.

Dr. R. Lessing said there was one point on which he would like to say a word, and that was the very interesting question of the carbon formation in the cracking experiments on paraffin wax, and on the other hand the absence of carbon formation during Berginisation. One point which the author had mentioned had been that very little carbon was formed in the first instance, but that as time went on carbon formation proceeded rapidly. He would like to hear whether Prof. Waterman had any suggestion to make on that point and whether it was possibly true that the carbon first formed actually acted as a catalyst for the decomposition of the paraffin wax or of the primary decomposition products. There was no doubt that the carbon formation was due to a secondary decomposition of the primary decomposition products of the original raw material. He had some ground for suggesting that in connection with some work which he had done,

not only on coal, but on other organic substances such as sugar and cellulose. In that case the addition of catalysts had certainly made an enormous difference in the carbon produced, and he thought it would be worth while investigating that point.

Dr. Dunstan had mentioned that there was a slight difference in the analysis of the paraffin wax used, and it might be interesting to know whether there was any mineral ash in it, even to a small extent. It was likely there was. Inorganic compounds added to organic substances influenced the carbon production on heating; he was speaking of heating either to temperatures of 400° or 500° or the higher one of 900°. In the case of sugar one could, by selection of the addition, produce at will sugar or coke to an extent varying from 20 per cent. to 5 per cent. The same held good in the case of cellulose, and in connection with coal one could vary the coke production by about 15 per cent. up or down. It might be possible that something like that had happened in the case which Prof. Waterman had quoted.

With regard to the dehydrogenation of naphthenes, that method had, of course, been tried. It had been originally brought forward by Zelinsky. During the war he (Dr. Lessing) had made the suggestion to the Explosives Department, and had actually been engaged on the work of dehydrogenating the residual spirit from T.N.T. manufacted by the "Shell" process. He had been extrusted with a considerable quantity of palladium; but his efforts had been unsuccessful, and he had not been able to produce toluene from the corresponding fraction of the spirit.

Mr. Gordon Pitt said that some of the material which was now coming to light, and which had been so materially added to in a new way by Prof. Waterman, might have an important bearing in another direction by throwing a very interesting sidelight on the question of the natural production of petroleum oils, in that in those experiments which were artificially conceivably reproducing the conditions under which oil might have been produced naturally, especially as regarded the information given as to the production of hydrocarbon from fatty vegetable and animal oils.

Prof. Waterman said it was not possible for him to answer in a detailed manner all the questions which had been put, and he would reply to them fully in writing.

He might say, however, that he and his colleague had endeavoured to experiment with Bergius's ingenious idea only in a scientific and not in a commercial way. They had had no interest in obtaining commercial results.

On the motion of the Chairman, a hearty vote of thanks was accorded to Prof. Waterman and his colleague, and the meeting terminated.

Prof. Waterman subsequently wrote in reply:—

With reference to the Chairman's remarks, the high pressure of nitrogen and of methane does not have the same effect as high pressure of hydrogen when we compare the specific gravity of the oil obtained, and of the residue of Engler distillation. The bromine value also varies.[1]

We are carrying out a systematical research on the influence exerted by different pressures of hydrogen, of nitrogen, and of mixtures of these two gases.

Our experiments prove that after carrying the hydrogenation experiment for a short time only (15 minutes) the gasoline yield was higher by cracking than by Berginisation, whereas after a longer time the gasoline yield is in favour of the Berginisation experiment. We are in agreement with the Chairman that this fact is important to the knowledge of cracking in connection with his remark that 15 minutes was about the time to which the material was exposed to conditions of temperature and pressure in many of the technical cracking operations.

The quality of the crude gas oil (degree of insaturation) which was cracked by the Chairman and his colleagues might differ much from the paraffin wax, and this perhaps may explain the different behaviour, namely, the slight increase in gravity immediately after the cracking temperature was reached.

In reply to Prof. Brame, "heavy hydrocarbons" are ethylene and other olefines. "Other hydrocarbons" are methane, ethane, etc.

We are now preparing larger portions of Berginised paraffin wax in order to isolate the different liquid and gaseous hydrocarbons.

In reply to Dr. Henny, the influence of the quantity of paraffin wax does exist: compare experiments No. 72 and 68. Our paper proves the scientific value of "Berginisation" and does not regard the commercial value of this method. This latter will depend from the market prices of coal, gasoline and so on, and it is possible that even during our research work, which has already occupied three or four years, this commercial value will change.

In reply to Mr. Shatwell, the bromine values in the paper are given in percentages by weight of bromine absorbed. These bromine values are more reliable than iodine numbers.[2]

In reply to Dr. Lessing, our paraffin wax practically contained no ash.

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[1] H. I. Waterman and J. N. J. Perquin, *Proceedings Koninklijke Akademie van Wetenschappen*, Amsterdam, 1924, **27**, 132, and *Journ. Inst. Petr. Techn.*, 1924, **10**, (45), 670.

[2] Compare H. I. Waterman and J. M. J. Perquin, *Recueil des Travaux chimiques des Pays-Bas*, 1921, **40**, 677, and *Journ. Inst. Petr. Techn.*, 1924, **10**, (45), 671.

Mr. W. J. Wilson subsequently wrote:—With reference to t comment made by the Chairman on the authors' analysis of th Rangoon paraffin used for their experiments, I desire to stat that ordinary Rangoon paraffin does not contain oxygen, at any rate not sufficient to be indicated by an ordinary ultimate analysis.

A representative analysis of this paraffin of solidifying point 58° C. is:—

Carbon	85·25
Hydrogen	14·75
Sulphur	Nil

which is practically in agreement with the theoretical composition.

An Introduction to the Tectonics of the Rumanian Oilfields.

By Lieut. G. C. Flower, R.N.R.

Introduction.

A considerable amount has already been written concerning the Geology of the Carpathians, and also on the subject of the foothill zones and their associated oilfields. This paper, in attempting to connect the crucial problems germane to both subjects, makes little claim to present much that is new, but it is hoped that the presentations of contemporary ideas on Carpathian nappetectonics, and their significance in problems of oilfield structures in Rumania, will be of value to those who are still without a clear conception of the unique geology of the region.

Hitherto much of the published information has appeared in a foreign language and is normally inaccessible to the average reader.

Such English publications as we possess, however, are often of a highly controversial character, and imply advanced geological theories and interpretations for their proper understanding.

The chief difficulty that the writer has had to overcome is the selection of really relevant matter and the exclusion of a maze of detail which has been one of the primary causes of past misconception.

In laying stress on the most plausible and generally conceded views, the writer admits to a guidance, but not necessarily to a bias, from his own work in the region in question.

Geographical and Geological Boundaries.—As is generally known, the Rumanian oilfields are situated on the external border of the Carpathian mountain chain, *i.e.*, from the foothills to the adjacent bordering plain.

The Carpathians are the eastern continuation of the Alps, and roughly speaking, extend from the Danube at Vienna in a huge arc eastwards to rejoin the Danube again at the Iron Gates.

The acute elbow of the Carpathian chain is at Buzau, where the chain swings from the North-South to the East-West direction.

Broadly speaking, it is at the foothills of this elbow where the largest known oilfields are situated.

Geologically, the northern external border of the Carpathians is limited by the old massif of Bohemia, the old plateaux of Volhynia, Podohia and Bessarabia, and in the south by the Dobrodjea and the prebalacanic plateau.

The internal border of the Carpathians swings round the big Hungarian plain or Parmonian depression; and along this margin are the remnants of young volcanic eruptions.

Physiographically we can subdivide the Carpathians into three separate zones:—

I.		II.		III.	
Internal.		External.		Plain.	
In the West.	In the East.	Internal.	External.	Rumanian Plain.	Moldavian Region.
Mesozoic and older crystalline rocks.	Oligocene Eocene Cretaceous	Miocene Oligocene Eocene	Pliocene Miocene	Quarternary Pliocene	Quarternary Sarmatic (Miocene).

From the tectonic point of view the Carpathians may be subdivided into three principal zones:—

(1) The *Dacic chain*, which is regarded as a continuation of the Central Alps.

(2) The *Flysch Carpathians*, forming the present high chain.

(3) The *Sub-Carpathians* (called after Mrazec, the "diapyre zone").

The whole of the Carpathian chain, like the whole of the Alps, are what the French call "pays de nappes," and the Germans "Deckeland."

Nappe Theories.—Before proceeding further it is necessary to explain what is understood on the Continent by the word "nappe" or "Decke."

Unfortunately, we have no adequate word in English, *recumbent folding*, being used of a somewhat similar structure regarded from a slightly different point of view.

By "nappe" we understand a series of formations thrusted for a considerable distance over other formations.

Under the above concise definition such a variety of structures are involved that it seems necessary to give fuller information than is perhaps strictly in proportion to the length of this paper.

To give an example of a typical nappe, even diagrammatically, presents great difficulty; the nature of its growth and ultimate form depends on many and varied factors.

Fundamentally, we can draw no line of difference between the folding of the ancient rocks of the Scottish Highlands, termed *recumbent folding* (recorded by E. T. Baily and others), and the Mesozoic and later folding of the Alpine and Carpathian chains, termed "*nappes*."

But suffice it to say that the Highland tectonics now exhibit such denuded skeletons, a large part of which have subsequently been subjected to many forces additional to those primarily responsible for their formation, that we have a less hypothetical problem when considering the history of living nappes of a more recent period.

A nappe for its formation requires several co-existing forces in operation, and its achievement is essentially the result of compound action; moreover the majority of Continental geologists (as opposed to many British geologists) invoke some plutonic force in addition to tangential pressure necessary to nappe formation.

A nappe from its commencement of formation must be well covered. It may be said to receive its motive force from all sides, providing one side is subjected to lesser pressure.

To explain the formation of a nappe, it is easiest to consider it under two phases:—

1. *The "geo-cause."*
2. *The growth.*

Actually both 1 and 2 work co-laterally, the growth of a nappe being essentially of a compound nature.

1. The prime or "geo-cause" of nappe formation is yet hypothetical. In the Alps (the best studied nappe region), Argand supposes their "geo-cause" to be due to a species of subterranean tidal wave acting both below and also on the older crystalline rocks.*

This wave carrying on it the younger formations, is subsequently checked in its lateral movement by the nearest horst or other resistant body (see figure 1).

The impact thus set up, the pressure of the wave still being exerted in the same direction, causes the wave to assume a new shape, which in its turn reflects on its overlying formations. *The line of consequent nappes bear a definite relation to this line of deep-seated obstruction.* Until this wave meets resistance, naturally only oscillations occur. It must also be borne in mind that these overlying sediments have a larger displacement than the core acting on them from below. The mechanism of nappe formation does not imply solely tangential pressure, but more a composition of "inclined upward," subsequent tangential and wedge-squeezing forces. (In the case of the Carpathians Mrazec attributes the nappe "geo-cause" to the fact that the geo-synclinal movement proceeds from the Carpathians.)

2. The subsequent growth of the nappe may be said to be a function of the degree of pressure to which it is subjected, in addition to the relative plasticity of the nappe forming materials.

Under great pressure a nappe is very nearly in a state of equilibrium, *i.e.*, there being little difference between the reactionary force below and the direct force above; the nappe, when in this state, may assume practically any shape, and will obey no known physical laws.†

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* Yet unpublished, but stated by Argand at the Brussels Geological Congress, 1922.

† For further reference, see Otto Wilckens, *Grundzuge der tektonischen Geologie.*

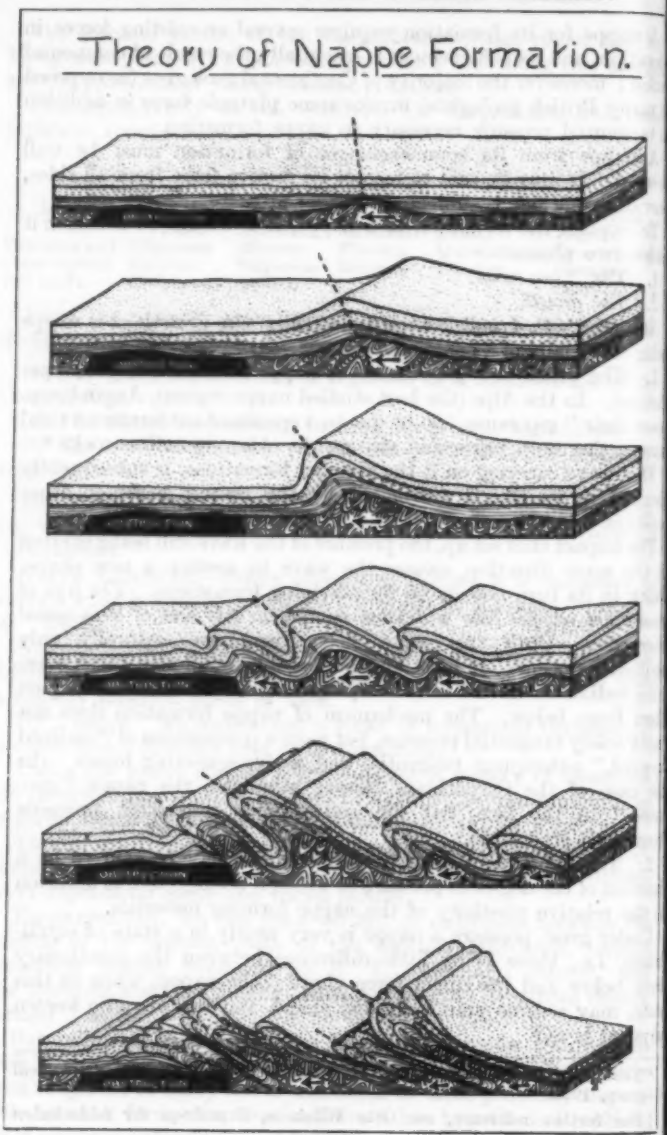


FIG. 1.

The rate of migration of pays de nappes *en masse*, depend entirely on the potency of the forces implied by the "geo-cause."

Their differential movement, growth and other characteristics, are entirely regulated by their different material being subjected to different pressures at different times. (In the Alps it is common for nappe 1 to over-ride nappe 2 or 3 or even more.)

Generally speaking, where one nappe is developed, others also occur. The movement of adjacent nappes is often more responsible than any other cause for the matured condition of any preceding nappe. Hence nappe formations may be described as being of compound growth.

One of the chief characteristics of nappe growth is the extraordinary degree of folding that can take place without fracturing, the nappe being for its greater part stratigraphically and tectonically complete between its planes of movement.

General Structure of the Carpathians.—The structure of the Carpathians is highly complex, and its elucidation is rendered more difficult by the fact that detailed studies, except in isolated regions, have not yet been carried out. This has naturally led to a great number of varied hypotheses. Further investigations have also shown that their intimate structure is even more complex than that of their larger and at first sight more contorted neighbours in the Alps.

Roughly, the constituent nappes of the Carpathians lie in approximately parallel zones, involving younger rocks the further such zones are removed from the interior of the arc. (This is a confirmation of Mrazec's theory that the Carpathian geo-synclinal axis is moving away from the central range itself. This also agrees with Argand's "wave theory.")

The Carpathian nappes are mostly of the "*scale*" type, not materially different from their Swiss counterparts, but with their under flanks highly laminated. Such flanks are often partially or completely squeezed out, laminated, or both.

Contrary to the general attitude of the Swiss nappes, the external nappes of the Carpathians usually have the external roots, while stratigraphically the same nappes usually involve the youngest sediments. In a sea generally regressional, these sediments have been deposited against the pre-existing highland.

Periods of Folding and Nappe Formation.—The study of the Carpathian nappes show three periods of folding (see Figure 2).

(a) Mesocretaceous.
(b) Miocene.
(c) Post-Pliocene.

Of these periods the first two were responsible for the formation of the seven nappes now constituting the Carpathian chain.

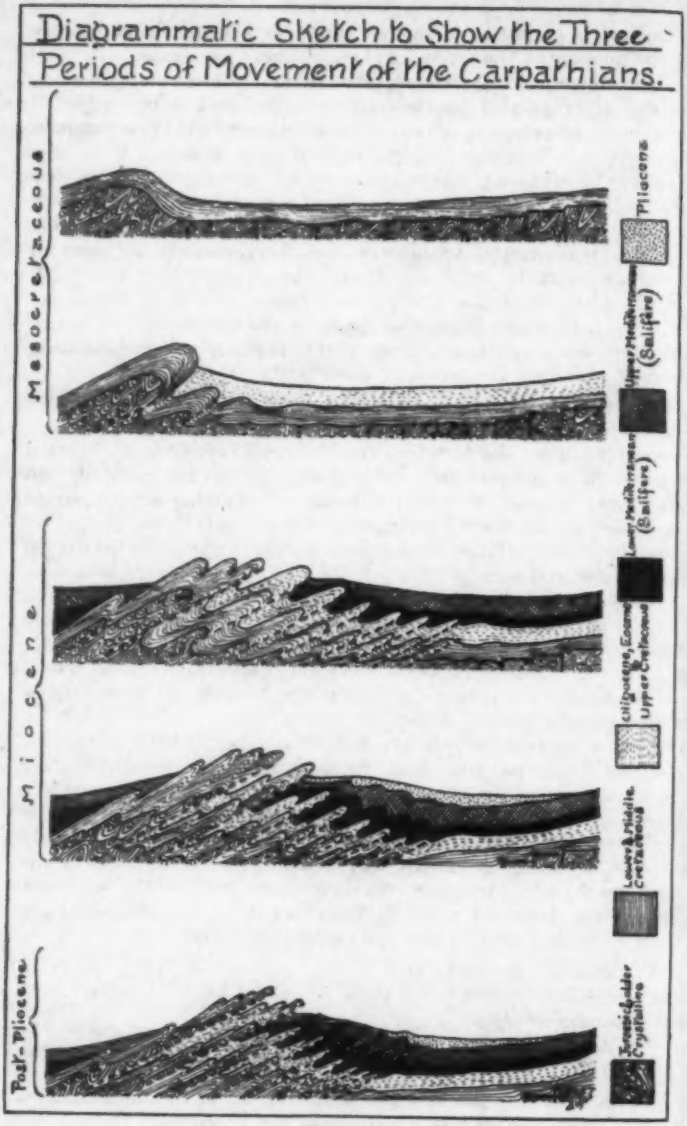

Diagrammatic Sketch to Show the Three Periods of Movement of the Carpathians.
Mesocretaceous
Miocene
Post-Pliocene
Pliocene
Upper Mediterranean (Salifère)
Lower Mediterranean (Salifère)
Oligocene, Eocene, Upper Cretaceous
Lower & Middle Cretaceous
Jurassic & older Crystalline

FIG. 2.

Commencing from the internal and oldest nappes there are:—

7. Getic (Murgoci).—This nappe is consequent on the first great period of folding (Mesocretaceous), and is composed of crystalline rocks of various ages.

6. Bucegi Conglomerate (P. Voïtesti).—This nappe, together with the succeeding six, results from Miocene folding. It is composed largely of material eroded from the Getic nappe and is incidentally responsible for the beautiful mountains of Sinaia.

5. Cozia.—Like the Getic nappe, this is deep-seated and is composed of crystalline rocks of various ages.

4. Sibiu (Mrazec).—This is chiefly made up of Upper and Middle Cretaceous limestone.

3. Senonian (P. Voïtesti).—This, on the authority of Popescu-Voïtesti, forms an independent nappe composed of red Senonian marls.

2. Fuzaru (P. Voïtesti).—This nappe is composed chiefly of Eocene sandstones, and limestones and marls.

1. Marginal (Mrazec).—This nappe is chiefly composed of Oligocene limestones and sandstones, and is the last matured nappe.

Salifère (Mrazec).—This series ("parautochtone") is composed of unique lagoonal, salt-impregnated sediments of Mediterranean (Suess) age (chiefly Miocene), the fringe of which is "implicated" in about the last four of these nappes. (See Figure 2).

The first great (Mesocretaceous) movement pushed the Carpathian geo-syncline outwards.

This geo-syncline was afterwards filled up with sediments in regressional seas depositing in order the Upper Cretaceous, the Eocene, and the Oligocene, showing younger and shallower sediments when ascending the series. The sediments were subsequently formed into nappes by the second great (Miocene) movement.

The Lower Miocene sea was transgressive and deposited a lagoonal facies with much gypsum and salt. This lagoonal facies is of great importance in connection with the oil formation and will be considered in the sequel.

The end of the second great (Miocene) movement saw the practical completion of the formation of the nappes.

The third (Post-Pliocene), although a rejuvenisation of the same movement, was quite insignificant as a nappe-moving factor, its only significance being due to its compressional force, not strong enough to move the old nappes further, but sufficient to cause a squeezing out of the most plastic sediments between its deep synclines (*i.e.*, the Salifère), or to cause it to "hurry before" the other material.

With the exception of the few nappe oilfields (of the Galician type), the situation of the whole of the so far known Rumanian

foothill oilfields are disposed in direct relationship to the tectonics derived from this last (Post-Pliocene) movement.

SALIFÈRE.—Before proceeding with the tectonics of the foothill structures, it is necessary to notice the behaviour of this Salifère, a curious facies which does not conform to the movements of its adjacent formations, though subjected to similar forces.

Salifère, however, is a misleading term, as the majority of that series probably possess only 2 or 3 per cent. of Salt, the isolated domes or horsts of practically pure NaCl responsible for so much controversy being of limited occurrence.

In this general paper it is impossible to discuss in detail the two opposing theories of its origin, (a) as a naturally deposited sediment, (Mrazec); (b) as a plutonic series of unknown age, making its way to the surface through lines of weakness in the earth's crust, (P. Voïtesti).*

It may be said that Mrazec's general principles are internationally acknowledged by the majority of geologists, and almost entirely by those personally acquainted with the Carpathian Salifère regions.

The Salifère series is chiefly composed of marls and shales; the more saline appearing to be derived from the first Mediterranean or lower Salifère.

The generally intrusive nature of the Salifère in relation to its adjacent formations, its intermixture with exotic material, its marked unconformity of deposition, its peculiarity of composition and lack of fossil evidence, have led some to regard it as other than a naturally deposited sediment of chiefly Miocene age.

The unique powers of saline series when intermittently affected by pressure and water, its alternating rigidity and plasticity, due to recrystallisation and other factors yet unsolved are quite responsible for its intrusive nature.†

The frequent occurrence of Salifère with exotic material (Jurassic and older) is both clearly and naturally accounted for when the history of the nappes' growth is appreciated. The over-riding nappes, in transit along their thrust plane, both sheer off and transport these older rocks from their deep-seated roots. (See figure 3). When once brought into contact with the Salifère, portions of this sheared-off debris are brought to the surface by the squeezing-out motion, before mentioned, to which the Salifère is subjected; its ascent to the surface is further assisted by the individual physical activity of the Salifère.

The unconformity between the Lower Salifère and the Oligocene is unfortunately mostly covered; at places, however, it is so slight

* The latter was dealt with in full in the English language in this journal, Vol. IX., No. 38, Aug., 1923.

† See Karl Gripp, "Steigt das Salz zu Luneburg, 1920."

FOOTHILL STRUCTURES.

The Pliocene foothill structures constituting over 90 per cent. of the Rumanian oilfields, broadly speaking, cover the Subfère like a blanket. (See Fig. 3.)

The constituent formations of the foothills are divided as follows :—

	Formation.	Oil bearing.	Approx. max. thickness.	Rock characteristics.	Water. S = Salt. B = Brackish. F = Fresh	Mode of deposition.	Characteristic fossils.
Upper Miocene.	Sarmatic ..	Poor ..	600 ft. ..	Limestones, marls and sandstones.	B ..	Marine ..	Cerithium, Mactra, Ervilia, Bulla, Trochus, etc.
Pliocene.	Meotic ..	Rich ..	1,300 ft. ..	Blue-green marls, sands and sandstones.	F to B ..	Marine and Estuarine. ..	Hydrobia, Unio, Neritina, Dosinia, Cerithium, etc.
	Pontic ..	Traces ..	2,300 ft. ..	Blue marls	S ..	Marine ..	Valenciennesia, Congeria rhomb. Cardium Lenzi, Vivapara, etc.
	Dacic ..	V. rich ..	1,200 ft. ..	Sands intercalated with thin marl bands and lignite.	F to B ..	Estuarine ..	Vivipara, bif., Prosodacna, Unio, Cardium, Dreissensia, etc.
	Levantine ..	None ..	2,100 ft. ..	Sands and gravel sometimes intercalated with thin marl bands.	F ..	Terrestrial and Estuarine. ..	Helix, Unio, Planorbis, etc.

that the "Menilith series" shales (Oligocene) often merge imperceptibly into similarly stratified shales of the Lower Salifère.

Its peculiarity of composition is understood when its lagoonal mode of deposition is taken into consideration. Also the lack of fossil evidence in such a saline sea would appear more natural than otherwise.

From the Petroleum geologists' point of view it is where the Salifère either totally or partially pierces or folds the Pliocene that oil accumulations are found.

Broadly speaking, in the foothills where the flexuring is greatest and the Salifère more active, the Pliocene has become completely pierced, exhibiting at the surface practically vertical horsts of Salifère. Further towards the plain, the Salifère becomes less active. This activity produces less pronounced structures, that is as so far known, gentle, regular anticlines and domes hidden under the diluvium of the Rumanian plain; these structures have yet only been explored by wells.

To describe a unique, though common structure of the Rumanian foothills, Mrazec has coined the term "*Diapyre*" fold. A Diapyre structure signifies a fold in a series into which Salifère from underneath has either partially or totally penetrated. (See Figure 3 (1)).

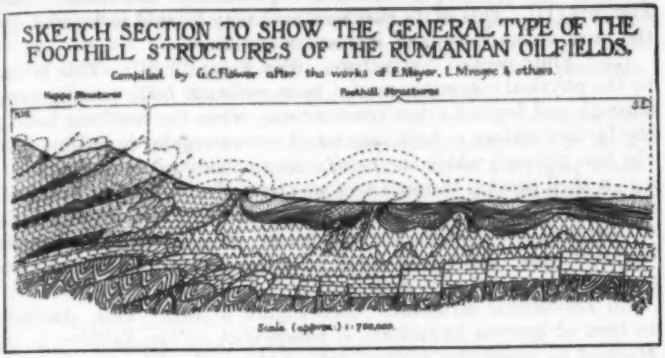
There are thus two distinct types of structure to be described, (*a*) where the Salifère has totally pierced its superincumbent sediments; (*b*) where it has simply formed them into a dome or anticline.

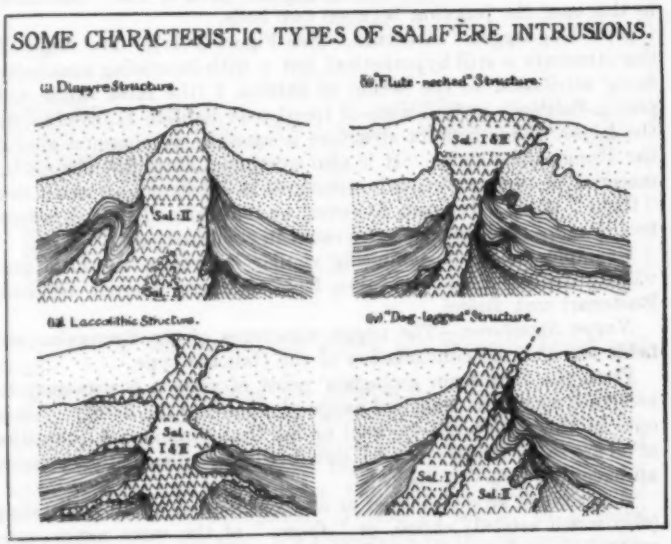
(*a*) The first type includes the most highly contorted strata, the relatively shallow Pliocene being often caught up and compressed between two parallel Salifère intrusions (See Figure 3), while further down the foothills the Pliocene is usually subject to acute asymmetrical folding.

(*b*) The second type conforms to normal anticlinal structures. Intermediate types, between (*a*) and (*b*) more of the simple Diapyre structure, are naturally frequent.

It will be well to take the opportunity of presenting here the most modern theories for some of the abnormally shaped Salifère intrusions, as met within drilling depth. It is on the mode of these intrusions that the structure of the Pliocene so greatly depends.

Before considering the varied characteristics of these intrusions as presented near the surface, their deep-seated geo-movement (*i.e.*, their squeezing-out action *en masse* from their nappes), and further, their interrupted passage of flow over an irregular—probably highly irregular—floor, must be kept in mind. The building forces probably responsible for Salifère intrusions are, initially, from the Salifère geo-movement; reinforced subsequently by the individual physical forces of the Salifère previously described.


SKETCH SECTION TO SHOW THE GENERAL TYPE OF THE FOOTHILL STRUCTURES OF THE RUMANIAN OILFIELDS.
Compiled by G.C.Flower after the works of E.Mayer, L.Mrazec & others.
Nappe Structures
Foothill Structures
NW
SE
Scale (approx.) 1:750,000.


SOME CHARACTERISTIC TYPES OF SALIFÈRE INTRUSIONS.
(i) Diapyre Structure.
Sal.: II
Sal.: I
(ii) "Flute-necked" Structure.
Sal.: I & II
(iii) Laccolithic Structure.
Sal.: I & II
(iv) "Dog-legged" Structure.
Sal.: I
Sal.: II

MESOZOIC Sedimentary Rocks
MESOZOIC & older Crystalline Rocks
(Structure Hypothetical)
OLIGOCENE
EOCENE
(Nappe Material)
SARMATIC
MEDITERRANEAN II
MEDITERRANEAN I
SALIFÈRE
MIOCENE
LEVANTINE
DACIC
PONTIC
MEOTIC
PLIOCENE

FIG. 3.

(1) Mrazec's Diapyre structure, previously described. (See Figure 3 (1)). This in its various stages may be said to be amongst the most common type of Rumanian structure.

(2) "Flute-necked" structure. (See Figure 3 (ii)). This is due to the physical consequence of a more resistant body passing quite through and beyond a less resistant one, when the resulting hole in the farther surface is both larger and more irregular in outline than the hole through which the more resistant body made its entrance; *e.g.*, a shell passing through armour-plate. In the case of a Salifère intrusion, it fills up the cavity thus produced. During the process of denudation, should the intrusion of the Salifère remain dormant, this "flute-neck" will be eroded away, exhibiting at the surface a simple "pipe-neck."

(3) Laccolithic structure. (See Figure 3 (iii)). This, similarly to that of igneous intrusions, is consequent on the Salifère, in its attempt to reach the surface, taking the path of least resistance, in this case the junction between two beds.

(4) "Dog-legged" structure. (See Figure 3 (iv)). The origin of this structure is still hypothetical, but is with increasing unanimity being attributed to the action of Salifère I (the most saline and plastic Salifère), in its excess of speed over Salifère II, over-riding the latter. This type of structure is exceedingly common among the Rumanian oilfields. It is also worthy of note that the exotic material (if present) in such structures is chiefly found along this "flight" plane. It must, however, be remembered that in nature two or more of these structures occur in combination.

Examples of fields exhibiting similar structures to those previously described may be taken from Campina, Moreni, Glodeni, Bustenari and Baicoi.

Nappe Structures.—The nappe structures of the Rumanian oilfields are a direct continuation of the Galician type.

From the Petroleum geologists' point of view it is necessary to ascertain where the Marginal nappe plunges into the Salifère. It is only in this (Oligocene-Eocene) nappe that commercial quantities of oil are so far found; the "Kliwa" (Oligocene) sandstone proving an excellent reservoir rock.

When much eroded, buried or closely followed by an over-riding (also much eroded) nappe, or "finger" of the same nappe, the recognition and elucidation of this Marginal nappe usually requires both detailed and intricate geological mapping.

In the Moldavia region, where the actual nappe oilfields are situated, the Pliocene, except for one local and small invasion, plays no part in the formation of the oilfields, other than obscuring some of its structures.

The Marginal nappe is thrusted for at least ten miles over (its "par-autochtone") the Salifère.

Evidence of the above stated conditions are clearly exhibited by the numerous Salifère *windows* met with throughout the entire nappe. In all probability this nappe has been thrusted quite twenty miles; but further westward the evidence of its prolongation is obscured by the absence of further *windows*.

Often the structure of the *windows* exhibits horsts of Salifère somewhat similar in character to those previously described in detail occurring in the foothill regions. Figure 4 shows a typical cross-section of the Moldavia nappe oilfield region. A peculiarity of this nappe is that in its transit it leaves a portion of its lower (Eocene) flank behind.* Space prevents further details being given of the many and varied complications met with in the Moldavian nappe region.

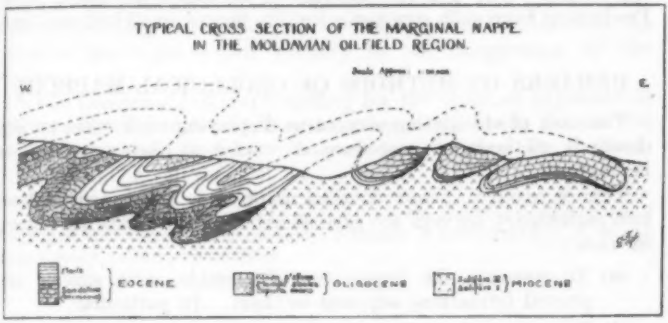


FIG. 4.

The existing oilfields in this region are Moinesti, Zemes and Solont.

Distribution of Petroleum in Relation to Tectonics.—Broadly speaking, in the productive formations, petroleum is found wherever structures suitable for its accumulation exist—quite irrespective of actual Salifère intrusions. Apart from its tectonic influence on super-incumbent formations, the Salifère has little geological claim to its universal association. Petroleum is also, to a small extent, distributed amongst the formations of the Mesozoic rocks.

In such greatly contorted structures as the Rumanian oilfields, migration of the petroleum has infinite scope. Also, unlike the oilfields of most other countries, the richest yields of petroleum are often obtained from the most contorted structures. In this respect another of the Salifère's peculiarities should be brought to notice:

* It should also be noted that subsidiary folding, over-thrusting and squeezing out occurs within the "fingering" or digitations of the nappe itself.

that its action of piercing its super-incumbent formations is contemporaneous with a sealing process on the lines of fracture thus made.

Thus, speaking generally, the largest Rumanian oilfields (at present located) are found where the productive formations are most raised.

The Salifère-made domes and anticlines of Pliocene, even the most gentle of them, also are often highly productive (providing the petroliferous formations are present). Some of these domes, however, yield more gas than oil.

In the nappe regions, oil accumulations are found either at the head or margin of the nappe where it plunges into the Salifère; also inside the nappe itself, where subsidiary and transversal folding at right-angles to the general structure of the nappe has taken place. Production from such structures usually proves small but constant.

REMARKS ON METHODS OF GEOLOGICAL MAPPING.

The task of elucidating structures displaying such wide variety demands methods of procedure as varied as the structures to be mapped.

Time is saved if, before detailed mapping is attempted, at least two preliminary surveys are carried out with the following objects in view:—

(*a*) To correlate the formations, if possible, with similar and proved formations adjacent to them. In particular,

(*b*) To assess the relative scale of the tectonic components, discriminating between the main, and the subsidiary or possibly secondary, features of the structure as a whole.

The practice, commonly advocated, of following out individual outcrops is here, in most cases, a hopeless procedure. Owing to the frequent pitching and swerving of fold-axes, to lamination, and to squeezing out, a single outcrop rarely reveals much consecutive evidence at the surface.

To meet this difficulty, variations of hypothetical structures are postulated to harmonise the proved junctions of the net structure, hypotheses being tested by longitudinal and cross-sections.

Actual Salifère intrusions may, of course, be treated as "inliers," their junctions being traced out in the usual manner.

Isolated observations of dip and strike, especially near Salifère intrusions, are to be regarded with the greatest caution: more often than not they are misleading. Similarly, and throughout the region, the utmost care is needed to detect secondary folding in a soft stratum bedded between more resistant strata. Such subsidiary folding is frequently exposed on a large scale. More-

over, the material which is now the most plastic was not necessarily so at the time of folding.

Conclusions.

(1) Without having first acquired a clear geological history of the unique geo-tectonics of the region, it is impossible to appreciate, let alone compare with other, the many and sometimes conflicting evidences brought forward to explain the peculiarities of the Rumanian oilfield structures.

(2) Although some of the explanatory theories here put forward may still be hypothetical, it is hoped that they may throw new light on the fantastic diagrams to be seen in some of our text-books—"cauliflower-like bodies without a root," "a section of a rabbit warren," etc.—all sharing one point of similarity, that the marginal lines of the diagrams are drawn so closely around them that the effective geo-cause is left entirely to the imagination of the reader.

While accepting full responsibility for the opinions expressed in this paper, the author desires to acknowledge with thanks the assistance received from his colleagues, Dr. M. Kraus, Dr. R. Noth, J. Slomnicki, E. Meyer, Dr. Krejci and H. B. Milner.

An article on the distribution of petroleum in the most important regions of Roumania will shortly be published by Messrs. J. Slomnicki and E. Meyer in an English technical periodical.

An Examination of the Refractive Indices of Motor Fuels with Regard to their Aromatic Contents.

By W. N. Hoyte.

An examination of the tables shows a very marked difference between the refractive indices of aromatic hydrocarbons and the indices of other hydrocarbons likely to occur in motor spirits.

The following are taken from Landolt's Tables.

Substance.	Refractive Index. D line.	Temperature at which observation was taken.
Pentane	1·36057 ..	13·1°
Hexane	1·37536 ..	20
2-Methyl pentane	1·37473 ..	15
Methylcyclohexane	1·42531 ..	15·5
Octane	1·4007 ..	15·1
2-Propylpentane	1·40131 ..	14·4
Decane	1·4108 ..	14·9
3-Ethyl tetradecane	1·43921 ..	14·2
Hepta decane	1·43583 ..	23·7
Dihydrobenzene	1·47555 ..	20
Tetrahydrobenzene	1·44507 ..	22·1
Pentene	1·4079 ..	18
Hexadiene 2, 4	1·45591 ..	12·5
Hexylene	1·39446 ..	23·3
2, 4-Dimethylpentadiene 2, 4 ..	1·44055 ..	17·3
Benzene	1·50144 ..	20
Toluene	1·4992 ..	14·7
o-Xylene..	1·5082 ..	14·1
m-Xylene	1·49962 ..	14·9
p-Xylene	1·4985 ..	14·7

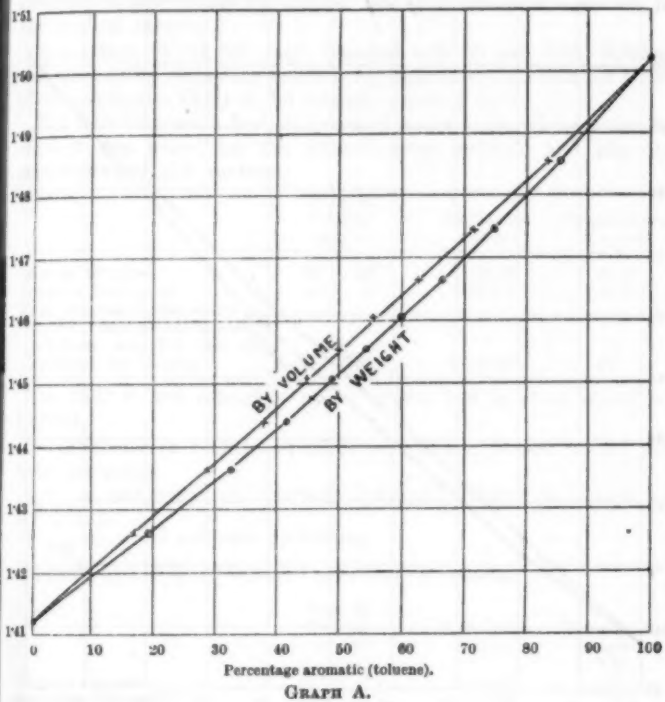
An examination of many brands of motor fuels in the refractometer confirms this observation—unless the natural fuels were blended with large amounts of aromatic hydrocarbons, their refractive indices never exceeded 1·43 at ordinary temperatures.

The influence of known percentages of aromatics from 0 to 100 was then observed as regards the refractive index of the mixture; the relations in two of the observations, which were typical, are shown in the accompanying graphs A and B. Graph A illustrates mixtures of heptane and toluene. Graph B mixtures of an aromatic free motor spirit and toluene.

It is seen that the relation for percentage of toluene by volume is almost a straight line, slightly concave downwards. The relation for percentage of toluene by weight is slightly more concave in the same direction.

In the observations a Pulfrich refractometer and a sodium flame were used throughout.

In order to obtain accurate and consistent readings it was necessary to determine the temperature co-efficient of the refractive index of several motor fuels, for without special thermostatic arrangements, the temperature at which observations were made



GRAPH A.

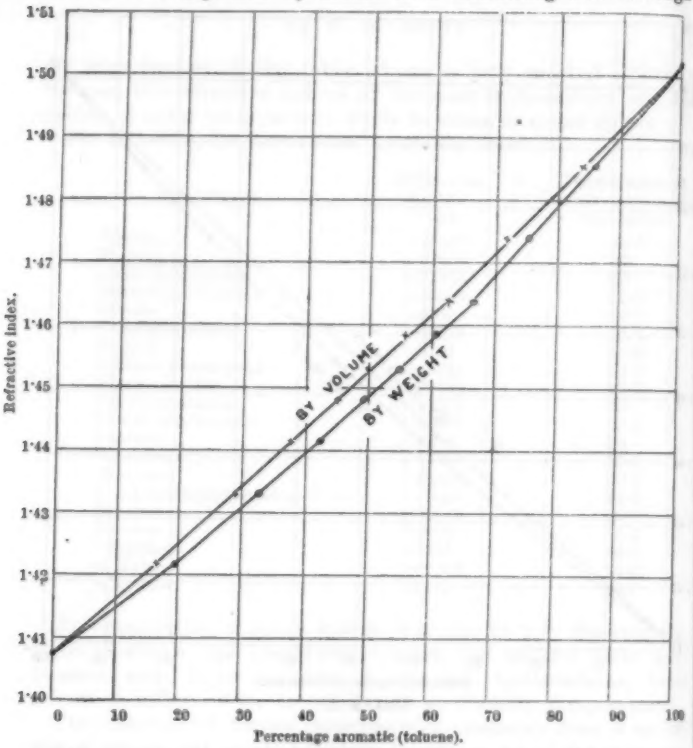
varies slightly, and as the co-efficient is large the results would have been affected accordingly.

Results were obtained as follows:—

Fuel A.	Sp. gr. 0·722	Difference in refractive index per ° C. rise in temp.	= 0·000425
B.	0·735		= 0·000499
C.	0·747		= 0·00042
D.	0·7215		= 0·00046
E.	0·762		= 0·00046

Difference in temperature of successive observations were anticipated to be only slight, or an average co-efficient of –0·00045 per °C rise in temperature; or –0·00025 per °F rise.

The refractometer required further slight modification to check evaporation, for with the standard equipment the lighter fractions evaporated, giving a steady rise in refractive index of the liquid. This was accomplished by means of a well-fitting cork through



GRAPH B.

which a thin copper tube passed; this carried a stream of tap water. A loop of the tube dipped into the fuel and thus served to bring it to a known temperature.

The method was then applied to determine the aromatic content of samples of various motor fuels. The refractive index of the sample was determined; a portion was then freed from aromatics by the standard method.

The refractive index of this aromatic free portion was then found. A known volume of a 50/50 mixture of benzene and toluene was added to a known volume of the aromatic free spirit or that the refractive index of the mixture was almost equal to that of the original sample. It was then a matter of simple proportion to calculate the percentage of aromatics by volume in the sample, and a short calculation converts this with sufficient accuracy to percentage by weight, knowing the specific gravity of the original sample.

A mixture of 50 per cent. benzene and 50 per cent. toluene was used as its refractive index is approximately a mean for those of the aromatics likely to be present in motor fuels.

The following are a few examples of motor fuels, whose aromatic content was found by the refractometer method, and also by means of the C.S.T. method.

	Fuel A. Critical angle.	Refractive Index.	Temperature of spirit. ° F.
Original samples	49° 26′	.. 1·42946	.. 46·5
Aromatic free spirit	50° 8′	.. 1·42524	.. 46·5
5 c.c. Aromatic free spirit plus 0.3 c.c. benzene, toluene 50/50 mixture, i.e., 5·7 per cent. aromatic by volume ..	40° 30′	.. 1·42906	.. 47

At 46·5° F. the refractive index of this last mixture would be 1·42918.

A difference of 1·42818—1·42524=0·00394 is caused by 5·7 per cent. aromatic.

*** A difference of 1·42946—1·42524=0·00422 is caused by $\frac{5{\cdot}7 \times 422}{394} = 6{\cdot}1$ per cent. by volume.

Result by C.S.T. method 5·7 per cent. by volume.

	Fuel B. Critical angle.	Refractive index.	Temperature of spirit. ° F.
Original sample	52° 7′	.. 1·41332	.. 51
Aromatic free spirit	54° 15′	.. 1.40063	.. 49
5 c.c. aromatic free spirit plus 0·8 c.c. benzene toluene 50/50 mixture, i.e., 13·8 per cent. aromatics by volume ..	52° 27′	.. 1·41133	.. 49

Refractive Index of Original Sample at 49° F.=1·41382.

∴ Percentage Aromatics by Volume=

$$\frac{(1{\cdot}41382-1{\cdot}40063) \times 13{\cdot}8}{1{\cdot}41133-1{\cdot}40063.} = 17{\cdot}4 \text{ per cent.}$$

Result by C.S.T. Method=17·2 per cent. by volume.

FUEL C.

	Critical angle.	Refractive index.	Temperature of spirit. ° F.
Original sample	52° 25′ ..	1·41153 ..	50·5
Aromatic free spirit	53° 59′ ..	1·40221 ..	50
5 c.c. Aromatic free spirit plus 5 c.c. benzene toluene 50/50 mixture, *i.e.*, 10·7 per cent. aromatics by volume ..	52° 18′ ..	1·41223 ..	51

Refractive Index. Aromatic Free Spirit at 50·5° F. = 1·40209.
Refractive Index. Artificial Mixture at 50·5° F. = 1·41235.
∴ Percentage of Aromatics by Volume =

$$\frac{(1{\cdot}41153 - 1{\cdot}40221) \times 10{\cdot}7}{(1{\cdot}41235 - 1{\cdot}40221).} = 9{\cdot}85 \text{ per cent.}$$

Result by C.S.T. Method = 10·3 per cent.

The method is quick and easy to work.

It is found most essential to wash out the cup on the refractometer with the spirit to be tested, to remove all traces of spirits previously tested.

After the final water wash in the removal of the aromatics by sulphuric acid, it is not found to be necessary to dry the spirit with calcium chloride for several hours, precisely the same refractive index is obtained before and after drying.

This method of determining the aromatic content of a fuel is open to the same objections as any other method, *i.e.*, the physical properties of the compounds other than aromatic, which are extracted by the acid are unknown. Nevertheless the method is quick and neat and on repetition gives results which agree extremely closely.

The Constitution of Asphalt.

By H. I. Waterman, Ph.D., and F. J. Nellensteyn, Ph.D.
University of Delft, Holland.

Experimenting with an artificial asphalt, obtained by oxidizing with air a Borneo asphalt-base oil of high boiling-point at a temperature of 300–350° C., one of the writers isolated "carbon" by a long continued extraction with various solvents successively: gasoline 40–60°, gasoline 60–80°, a mixture of gasoline 60–80° and CCl_4(1 : 1), CCl_4 and C_6H_6,[1] and on this fact and other experiments founded a new theory on the constitution of asphalt, leading to the conclusion that colloidal carbon is the essential substance of asphalt.

At a later date these researches were extended to *natural* asphalts, namely, Trinidad asphalt, Neuchâtel asphalt (Val de Travers), and Italian rock-asphalt. The mineral constitutents of these asphalts were largely removed by boiling with benzene and centrifuging the non-soluble particles. After evaporation of the benzene on a steam-bath the asphalt was subjected to an extreme extraction with the solvents above mentioned. Trinidad asphalt certainly gave a carbon, which may be supposed to be a coagulated or flocked product and not a chemically formed carbon, for during the treatment the temperature never exceeded 100° C. Until now we have not obtained similar good results with Neuchâtel and Italian asphalt, although we stated, that the solubility in benzene of the final product had largely decreased. Generally we found that the velocity of solution of these asphalts decreased with the rate of the extraction. So often after extraction heating was necessary to get the product dissolved, while without any treatment the original product easily dissolved at room-temperature.

Moreover carbon was obtained from a Belgian artificial coal-tar asphalt, obtained by oxidising with air (from the coking-plant at Strépy-Bracquegnies, Belgium). From this asphalt the "free carbon" was removed by extraction with benzene and evaporation of the benzene on a steam-bath. "Carbon" was obtained from this asphalt by extraction with gasoline 40–60° and æther;

[1] F. J. Nellensteyn, The Constitution of Asphalt, *J. Inst. Petr. Techn.*, 10, 311 (1924).
For more particulars vide: Bereiding en constitutie van asphalt, Diss. Delft, 1923.

especially this latter solvent gave very good results with coal-tar asphalts. The analysis of the carbon was:—

H 5·35 and 5·2 per cent.
C 91·0 and 91·4 per cent.

The carbon from Trinidad Asphalt appeared to contain mineral substances, notwithstanding that the crude Trinidad asphalt had previously been extracted with benzene. The small quantities of inorganic matter evidently accumulated in the extraction residue, as extraction proceeded, and the carbon became more insoluble.

Of the treated asphalts, carbon is most easily coagulated from coal-tar asphalt; then follows Trinidad asphalt, while the Swiss and Italian asphalts at our disposal evidently belong to very stable colloidal solutions of "carbon." We wish to express our thanks to Mr. A. J. P. van den Burgh, who did the experimental part of this work.

STUDENTS' SECTION, LONDON BRANCH.

THE EIGHTH ORDINARY MEETING of the Students' Section, London Branch, was held at Aldine House, Bedford Street, London, W.C. 2, on Tuesday evening, October 21st, 1924.

MR. R. F. OWEN, the Chairman, called upon MR. GARLICK to read his paper, an abstract of which follows :—

An Outline of the Present State of Knowledge regarding "The Chemistry of Petroleum."

BY H. S. GARLICK (Student Member).

Summary.

1. The paper deals in the following order with the Chemical Constitution of Petroleum in general, dealing with fields in which paraffin hydrocarbons, benzine hydrocarbons and naphthenes respectively predominate.

Difficulties met with in isolating pure compounds and methods of attack.

2. More detailed account of the chemical compounds isolated from petroleum, under the following classes :—

1. Paraffin Hydrocarbons—Natural Gas and Paraffin Wax.
2. Saturated Monocyclic Naphthenes.
3. Polycyclic Naphthenes—Lubricating Oils.
4. Unsaturated Hydrocarbons—the Olefines.
5. Benzenoid Hydrocarbons.
6. Sulphur and Sulphur-containing Compounds.
7. Nitrogen Compounds.
8. Organic Acids—the Naphthenic Acids.
9. Asphaltic Matter.
10. Colouring and Fluorescent Bodies.
11. Organic Ash.

Under these classes, individual compounds are briefly referred to, and occasionally their reactions and/or methods of synthesis, and future commercial use to which they might be put.

3. Conclusions—Methods to be adopted, etc. References to important work done.

Petroleum.—Since much of the earlier chemical work on petroleum was carried out with distillates of light Pennsylvanian oil it is often erroneously stated that "American" petroleum consists of paraffins, whilst on the other hand "Russian" petroleum

consists of naphthenes and polynaphthenes. Generally, however, it may be said that the petroleums of no two producing regions are the same. Few petroleums consist mainly of hydrocarbons of the paraffin series, C_nH_{2n+2}, but the lighter, low boiling fractions of most petroleums consist of these hydrocarbons almost exclusively. Although the petroleum typical of the Pennsylvania field probably contains the largest percentage of paraffins, the higher boiling viscous fractions of this crude contain but few per cent. of these hydrocarbons, and these are removed by chilling, thus manufacturing the "paraffin wax" of commerce. The remaining lubricating oil consists chiefly of hydrocarbons of the class C_nH_{2n-2}, but their structure is unknown and no pure individuals have been isolated from them. Vaseline derived from Pennsylvanian petroleum is a mixture of hydrocarbons of the empirical formula C_nH_{2n-2} and C_nH_{2n-4}. Petroleums from certain American fields contain no paraffins, for example Coates[1] has shown that the lightest distillates of the oil from the Jennings, Louisiana, field consist exclusively of cyclic hydrocarbons of the C_nH_{2n} series.

The number of hydrocarbons which have been isolated from petroleum is comparatively small.

All American petroleums which contain large proportions of lighter distillates, as in the case of the light Appalachian, the Mid-Continent, and the North Texas crudes, yield gasoline and kerosene consisting chiefly of paraffin hydrocarbons. Low-boiling distillates, consisting of cyclic hydrocarbons or naphthenes, are usually derived from heavier crudes, as for example the heavier California, and the Jennings, Louisiana, crudes, from which Coates has isolated the dicyclic hydrocarbons $C_{10}H_{18}$ to $C_{12}H_{24}$.

Beilstein and Mibatow[2] have shown that the more volatile hydrocarbons of Russian petroleums possess the empirical formula CnH_2n and exhibit none of the reactions of olefines. In general their properties resemble those of the hydrocarbons of the Methane series. Two hydrocarbons of Formula C_6H_{12}, one boiling at 72° C. and the other at 80° C., were isolated. Cyclohexane prepared by Baeyer proved identical with the later hydrocarbon, and it was shown that the isomeric hydrocarbon was methyl cyclopentane. Evidence of the presence of cycloheptane in the fraction, boiling-point 115-120° C., of Caucasian oil has been obtained.[3]

Aromatic or benzenoid hydrocarbons have been found usually in very subordinate proportions in all petroleums that have been carefully examined.

Conclusion.—One of the most urgent of problems in this study is the necessity of checking the recorded physical properties of already

[1] *J. Amer. Chem. Soc.*, **28**, 384, 1906.
[2] *Ber.*, 1880, 13, 1818; 1889, 307, 342.
[3] *Ann.*, 1898, 301, 154; 1898, 302, 37.

identified compounds. These vary so much that it is difficult to draw any conclusions from present data. Simple derivatives of hydrocarbons are frequently known in a much purer state, and the physical properties detailed with much greater accuracy, than the parent hydrocarbons themselves. Tables of the physical constants, even of the simple paraffins, vary widely. For instance, the figure given for the melting-point of normal octane is 98·2, whilst Fororand[4] in a recent determination states it to be 57·4. Very few of the unsaturated hydrocarbons are known in a state of purity, and the constitution of them is still in doubt. The same may be said of the naphthenes. Most of the individuals described are evidently mixtures of two or more hydrocarbons.

A discussion followed, in which Messrs. J. B. Kay, E. Clark and T. G. B. Davies took part, and the Author replied to the questions raised.

[4] *Compt. Rend.*, 1921, 173, 31.

STUDENTS' SECTION, BIRMINGHAM BRANCH.

The NINTH ORDINARY MEETING of the Birmingham Branch of the Students' Section was held at the University of Birmingham on January 27th, 1925, and an abstract of the paper which was read follows.

Fire Problems in the Oilfields and Refineries.

By G. COTTON (Student Member).

AT least two million pounds are lost annually through oil fires, the majority of which are caused by lightning. Over a period of 10 years lightning accounted for 62 per cent. of the oil fires in the U.S.A.

On the question of protection against lightning it is generally agreed that lightning conductors on oil tanks themselves are not desirable, but they should be placed in a ring round the whole of the tanks, or one placed centrally at a good height above the tanks. Another method in use is to provide elongated points on the tanks and so relieve the tension in the atmosphere.

A cause of danger in steel tanks is the vent pipe by which inflammable gases are allowed to escape into the air, as these gases are liable to be ignited by a lightning flash or even by a small subsidiary spark. Flame may be prevented from entering the tank by fixing a gauze over the end of the pipe, or better still by leading the gases direct to an adsorption plant.

The best protection in the case of oil reservoirs is an all-steel tank, not specially earthed, and the prevention of vapour escaping into the atmosphere.

A device for the prevention of evaporation is the movable roof tank, the chief advantage of which is that it leaves no air or vapour space above the oil.

Static electricity has been the cause of many disasters and may be generated by the band-wheel belt or other moving parts of a rig. This may be prevented by earthing all machinery and providing belts with copper brushes connected to earth. Bull and calf wheels should be provided with a water spray, and boilers should be placed so that they will not be a danger to a flowing well.

The electric lamp is much safer than any form of lighting where gas may be encountered, but the breaking of the bulb may bring the gas into contact with the filament, which glows at a high temperature, although in some cases the inrush of gas destroys the filament. A series of tests carried out by the U.S. Bureau of

Mines showed that all standard sizes of carbon filament lamps ignited the gas at least once by breaking off the tips of the bulbs, and all standard carbon filaments, except those rated 8 candle power, 220 volts, ignited the gas when the bulbs were broken by smashing. Tungsten filament lamps were found to be much more dangerous than carbon filaments. It appeared that the best lamp for lighting in gaseous places is the 8 candle power, 220 volts, carbon filament, with bulbs constructed without a tip. Wiring should be carried in iron pipe conduits, and switches, etc., kept away from the danger zone.

Methods of extinguishing fires may be divided into three classes : (*a*) by excluding air ; (*b*) by preventing fuel getting to the flame ; and (*c*) by reducing the heat below ignition temperature.

For the extinction of gas fires steam is generally used. Various types of " snuffers " are also used for extinguishing gas fires, most of which act on the general principle of a large diameter pipe, fitted at one end with a valve and lower down with two or more valves from which branches lead away out of the danger zone. This is placed over the fire with the top valve open ; the top valve is then closed and the side ones opened, breaking the flow of the gas and extinguishing the fire.

The usual chemical extinguishers involve the use of sodium bicarbonate and sulphuric acid, but are not frequently used for big fires. Carbon tetrachloride is often recommended for use, and when applied to oil fires tends to extinguish the fire by mixing with the oil and diluting it, and also forms a blanket of non-combustible gas which excludes the air.

Tank fires may be fought with steam fed into the top of the tank, but frothy mixture systems are best for these fires. Essentially these provide for the bringing together of two chemical solutions which combine to form a thick tenacious foam, which spreads over the surface of the burning oil and excludes the air. The important point in regard to the use of foam is that it not only extinguishes but also prevents re-ignition. This system has been approved by the Board of Trade as a means of extinguishing fires on board ship.

Tanks should be surrounded by a dyke of sufficient height to hold more than the capacity of the tank, and should have large suction pipes so that in case of fire as much oil as possible can be removed to other tanks.

Stills and other apparatus in refineries should be surrounded by concrete or brick fire walls, thus dividing the entire installation into small areas in which fires may be localised, and high walls should be built between benches of stills to prevent flames being carried by the wind. A high-pressure water system should be

maintained and hydrants, with at least 2½-in. outlets, installed at convenient positions.

Mr. C. J. Ward and Mr. Dunstan took part in the subsequent discussion, the latter pointing out that fires are often caused by carelessness and disregard of rules as to smoking, etc.

REVIEWS.

"Carbonisation of Coal in Continuous Vertical Retorts." A South Wales Gas Coal. Fuel Research Board, Technical Paper No. 10, pp. iv. + 26, 1 pl. H.M. Stationery Office. 1s. net, postage extra.

Gives the results of an investigation carried out at the Fuel Research Station on samples of coal from the Meiros Colliery, Llanharan, consisting of approximately 60 per cent. Pentre seam and 40 per cent. No. 3 Rhondda seam.

Full details of the tests, which were carried out in four continuous vertical retorts on the Glover-West system, are given. Three full scale tests, each on 50 tons of coal and 120 hours duration, were made using 5, 12.5 and 20 per cent. of steam respectively, and tables are appended showing temperatures and pressures, analyses of raw material and products, and yields and weight balance, a diagram of the plant being also included. G. S.

"Outlines of the Occurrence and Geology of Petroleum." I. A. Stigand. (With an Appendix on Geo-physical Methods as Applied to Oil-Finding, by M. Mühlberg, Ph.D.). Pp. X. + 246. London: Charles Griffin and Co., 1925. 10s. 6d. net.

This little book forms a useful and up-to-date volume to be added to those works on petroleum that we already owe to the enterprise of Messrs. Charles Griffin and Co., Ltd.

The title aptly describes the contents, and no student of petroleum technology—and we are all students—can fail to derive benefit from its perusal. The science of petroleum in its present barely adolescent stage bristles with controversial subject matter, and we should have preferred to see the second chapter ("The Origin of Bitumen") at the end of the book. There is so much solid matter embodied in succeeding chapters that it seems a pity at the outset to recite the varied origin-hypotheses at so early a stage, and the conclusions drawn would surely have more force when viewed in the light of their useful and varied information contained in the body of the work. It is, however, a very ably written chapter.

Another subject, always a bugbear to the student of rocks and minerals, is that of classification; this is fitly reserved for the concluding chapter, which gives a most admirable summary of current news in the section, "Solid Hydrocarbons and Bitumens"; this should prove most useful for purposes of reference. Time alone can bring even comparative agreement upon these matters of classification and nomenclature.

The collation and co-ordination of facts from varied sources that bear upon such subjects as "The Accumulation and Concentration of Petroleum" are suggestively treated. The same may be said of the following chapter on "Problems in Movement and Accumulation."

The accumulations are classified under various headings and excellent diagrams and photographs illustrate many of the cases cited. "Oil-reservoirs" are next described, and finally there is a chapter on "Direct Indications of Petroleum," concluding with the summary already referred to of various solid forms of hydrocarbons.

Mention should also be made of Chapter III, dealing with the stratigraphical distribution of petroleum; a very useful table is given showing

the order of succession as applied to stratified rocks in Europe, with British and foreign equivalents.

The summary regarding the remarkable association of certain strata (*e.g.*, Mid-Tertiary) with petroleum is important, although the explanation is yet awaiting us. This is one of the many problems touching the mode of origin.

The Appendix concludes the volume. This will be read with great interest by all who are concerned in locating oil under difficulties, as in new fields where structural and other features are hidden by an overburden.

The value of these Geo-physical methods seems to be passing out of the region of the nebulous into the clear light of practice in the field. Actual consideration of the methods employed is of too recondite a nature to be attempted in the present connexion ; that they will justify their employment will be the devout wish of everyone interested in the development of the petroleum industry. J. E. M. H.